

LABORATOIRE DE PHYSIQUE
DE L'ÉCOLE NORMALE
SUPÉRIEURE



T H E S E

présentée

à l'Université de PARIS VII

pour l'obtention du titre

de

Docteur es Sciences Physiques

par

Jean-Pierre NADAI

Sujet : Etude de l'oxydation anodique du tantale, de l'aluminium et du silicium
au moyen de la microanalyse par l'observation directe de réactions nucléaires.

Soutenue le 17 mai 1971 devant la commission d'examen :

MM. P. NOZIERES	:	Président
G. SLODZIAN	:	Examineurs
P. CHEVALLIER	:	
G. AMSEL	:	Invités
G. FEUILLADE	:	

T H E S E
présentée
à l'Université de PARIS VII

pour l'obtention du titre
de
Docteur ès Sciences Physiques

par
Jean-Pierre NADAI

Sujet : Etude de l'oxydation anodique du tantale, de l'aluminium et du silicium
au moyen de la microanalyse par l'observation directe de réactions
nucléaires.

Soutenue le 17 mai 1971 devant la commission d'examen :

MM. P. NOZIERES	: Président
G. SLODZIAN	: Examineurs
P. CHEVALLIER	
G. AMSEL	: Invités
G. FEUILLADE	



Ce travail a été effectué au Laboratoire de Physique des Solides de l'Ecole Normale Supérieure.

Je tiens à remercier Monsieur le Professeur Y. ROCARD d'avoir bien voulu m'y accueillir.

Je remercie Monsieur le Professeur P. NOZIERES, Directeur du groupe de Physique des Solides de l'Ecole Normale Supérieure, pour l'intérêt qu'il a porté à ce travail.

Monsieur G. AMSEL, Directeur de Recherches au C.N.R.S., a dirigé ce travail. Ma formation de chercheur doit beaucoup à son enseignement d'une grande rigueur scientifique. Je suis particulièrement heureux de pouvoir le remercier ici pour les encouragements, les conseils précieux, l'aide constante et amicale qu'il n'a cessé de me prodiguer.

Je prie Messieurs les Professeurs P. CHEVALLIER et G. SLODZIAN, qui m'ont fait l'honneur de juger mon travail, d'accepter l'expression de ma respectueuse reconnaissance.

Durant son séjour au laboratoire de l'E.N.S.; Monsieur G. FEUILLADE s'est intéressé à ce travail et fut ainsi l'initiateur de plusieurs expériences. Qu'il trouve ici l'assurance de ma profonde reconnaissance.

Au moment où je tiens à exprimer ma gratitude à tous mes camarades de laboratoire auprès desquels j'ai toujours trouvé un excellent esprit de coopération, je voudrais remercier tout spécialement Messieurs J. SIEJKA et C. CHERKI pour leur collaboration amicale et leur contribution constante et décisive à la réalisation et à l'interprétation des expériences.

Je voudrais remercier également Monsieur M. CROSET de la Sescosem pour sa collaboration précieuse à ce travail.

Je ne saurais oublier la précieuse collaboration de Messieurs E. d'ARTEMARE, E. GIRARD, J. MOULIN, J.P. ENARD, B. LAVERNHE et J. RIVIERE. Je voudrais qu'ils trouvent ici, ainsi que tous ceux qui, à titres divers, m'ont permis de mener à bien ce travail, l'expression de mes plus vifs remerciements.

TABLE DES MATIERES

	Pages
<u>Introduction</u>	1
<u>I Principes de la microanalyse nucléaire</u>	2
A - <u>Détermination de la quantité de noyaux au voisinage de la surface de l'échantillon</u>	2
B - <u>Détermination de profils de concentration</u>	3
C - <u>Microanalyse par rétrodiffusion coulombienne</u>	4
<u>II Application de la microanalyse nucléaire à l'étude de l'oxydation anodique de l'aluminium, du tantale et du silicium</u>	6
A - <u>Sans marquage à l'O¹⁸</u>	6
1° <u>Mesure d'épaisseurs équivalentes</u>	6
a) <u>Lois de croissance de films d'oxyde anodique</u>	6
b) <u>Vitesse de dissolution</u>	7
2° <u>Détermination du rendement faradique de l'oxydation</u>	7
3° <u>Stoechiométrie et incorporations</u>	8
4° <u>Détermination du rendement en oxygène et des mécanismes d'incorporation</u>	9
B - <u>Marquage à l'O¹⁸</u>	10
1° <u>Les sources de l'oxygène</u>	10
2° <u>Echange isotopique</u>	11
3° <u>Mécanisme de transfert de l'oxygène au cours de la croissance du film d'oxyde</u>	13
<u>Conclusion</u>	15

Introduction

L'observation directe de réactions nucléaires induites par des particules chargées est particulièrement bien adaptée à l'étude des phénomènes de surface. Cette méthode de microanalyse permet de déterminer avec une grande sensibilité la quantité d'éléments légers (ainsi que d'éléments lourds dans des cas favorables) à la surface des solides. De plus cette méthode permet de localiser ces éléments en fonction de la profondeur avec une résolution inférieure au micron.

Le développement de cette méthode de microanalyse et son application à l'étude de l'oxydation anodique de l'aluminium, du tantale et du silicium est l'objet essentiel de ce travail qui a donné lieu à quatre publications :

- 1) G. Amsel, J. P. Nadai, E. D'Artemare, D. David, E. Girard et J. Moulin (1971) Nucl. Instr, and Methods, sous presse.
- 2) J. Siejka, J. P. Nadai et G. Amsel (1971), J. Electrochem. Soc., sous presse .
- 3) G. Amsel, C. Cherki, G. Feuillade et J. P. Nadai (1969), J. Phys. Chem. Solids , 30, 2117 .
- 4) M. Croset, E. Petreanu, D. Samuel, G. Amsel et J. P. Nadai (1971), J. Electrochem. Soc., sous presse.

Dans ce qui suit, nous présentons une synthèse du travail qui a été accompli en nous référant aux résultats mentionnés dans ces quatre publications. Une extension de ce travail portant sur la théorie de l'interaction particule-matière est décrite en annexe.

I Principes de la microanalyse nucléaire

La méthode sera décrite ici très brièvement. La référence 1 donne une description très détaillée de la technique expérimentale de cette méthode. Au moyen d'un accélérateur Van de Graaf de 2 MeV, on envoie des particules chargées (protons, deutons, etc.) d'énergie comprise entre 600 keV et 1 500 keV, sur un échantillon ; le diamètre du faisceau est généralement de l'ordre du mm. Les particules chargées (protons, alphas, etc) issues des réactions nucléaires produites sur les éléments légers au voisinage de la surface de l'échantillon sont détectées au moyen de détecteurs à semiconducteurs. Des films de Mylar d'épaisseur bien choisie arrêtent les particules rétrodiffusées et permettent ainsi une détection des particules issues des réactions nucléaires pratiquement sans bruit de fond. Les réactions nucléaires donnent des particules monoénergétiques ; ainsi les pics apparaissant dans le spectre d'énergie des particules détectées, sont caractéristiques des noyaux présents dans la cible. Dans certains cas il peut être plus utile de détecter les rayons γ ou les neutrons plutôt que les particules chargées. Dans d'autres cas (microanalyse d'éléments lourds sur substrat léger, etc) c'est la rétrodiffusion élastique des particules chargées (He^4 , C^{12}) que l'on utilisera.

A - Détermination de la quantité de noyaux au voisinage de la surface de l'échantillon

Lorsque l'énergie de bombardement E_0 est au voisinage d'un plateau de la section efficace différentielle $\sigma_{\theta}(E_0)$ de la réaction, pour un angle de détection θ , on a, pour un écart ΔE_0 donné, $\sigma_{\theta}(E)$ sensiblement égale à $\sigma_{\theta}(E_0)$ pour E compris dans l'intervalle $[E_0 - \Delta E_0, E_0]$. Ainsi pour une profondeur x dans la cible, pour laquelle la perte d'énergie du faisceau est plus petite que ΔE_0 , soit pour $x < x_0$, $\sigma_{\theta}(E)$ peut être considéré comme constant. Si les noyaux analysés sont tous contenus dans le voisinage de la surface de l'échantillon ($x < x_0$), le taux de comptage $N(E_0)$ des particules issues de la réaction nucléaire considérée est donnée par :

$$N(E_0) = K i \sigma_{\theta}(E_0) \Omega \int_0^{x_0} C(x) dx$$

où K est une constante, i le courant du faisceau de particules incident, Ω l'angle solide de détection et $C(x)$ le nombre de noyaux (sur lesquels on observe la réaction nucléaire) par cm^3 à la profondeur x . La quantité

$$q = \int_0^{x_0} C(x) dx$$

est le nombre total de noyaux au voisinage de la surface ; q est exprimé généralement en atomes / cm^2 ou en mg/cm^2 . La valeur absolue de q est obtenue par comparaison avec des cibles de référence.

Le tableau II de la référence 1 donne les conditions expérimentales pour la microanalyse des noyaux O^{16} , O^{18} , N^{14} , F^{19} , C^{12} et H^2 ainsi que les taux de comptage obtenus pour des films contenant 10^{16} atomes / cm^2 . Rappelons que la précision relative obtenue, lorsque l'on détecte N particules, est $1/\sqrt{N}$. Ainsi une précision de 1% requiert une détection de 10^4 coups. Une telle précision est couramment obtenue en quelques minutes de comptage.

La réalisation de cibles de référence est un problème essentiel pour la microanalyse nucléaire. L'oxydation anodique du tantale [3] permet d'obtenir des cibles minces dont la teneur en O^{16} ou en O^{18} est parfaitement connue, ces cibles constituent donc d'excellentes cibles de référence pour l' O^{16} et l' O^{18} .

B - Détermination de profils de concentration

Le profil de concentration $C(x)$ peut être déterminé par deux méthodes. Pour des profondeurs de l'ordre de quelques microns, l'analyse du spectre d'énergie des particules issues de la réaction nucléaire permet de déterminer le profil $C(x)$ avec une résolution de l'ordre de $0,2 \mu\text{m}$ [1]. Cette résolution est fixée par la résolution en énergie du détecteur et par la dispersion en énergie des particules lors de la traversée de la couche d'épaisseur x de la cible et de l'absorbant (mylar) destiné à arrêter les particules rétrodiffusées.

Pour les cas où il existe une résonance fine de la section efficace $\sigma(E)$, la courbe $N(E_0)$ donnant le nombre de toutes les particules

issues de la réaction nucléaire en fonction de l'énergie de bombardement E_0 au voisinage de l'énergie de résonance E_R donne des informations quant au profil $C(x)$. Si E_0 est supérieure à E_R , les particules, perdant leur énergie dans la matière, auront l'énergie E_R au voisinage d'une profondeur x_0 . Le taux de comptage sera alors proportionnel à $C(x_0)$. On voit donc que la courbe d'excitation $N(E_0)$ est en fait une image de $C(x)$, donnée par la relation :

$$N(E_0) = \left[\int_0^{E_0} \left(\sigma_G(E) \int_0^\infty C(x) g(E_0, E, x) dx \right) dE \right] \times \text{Constante}$$

où $g(E_0, E, x)dE$ est la probabilité pour qu'une particule incidente d'énergie E_0 (qui est en fait la valeur moyenne de la distribution en énergie du faisceau incident) possède à la profondeur x , une énergie comprise entre E et $E + dE$. La détermination de cette fonction $g(E_0, E, x)$ et le calcul théorique de $N(E_0)$ pour un profil $C(x)$ donné est l'objet d'un travail qui, n'étant pas encore publié, est présenté en annexe. Toutefois, il est possible d'obtenir, sans faire une analyse mathématique poussée, des informations qualitatives à partir de la forme de cette courbe d'excitation $N(E_0)$ [1, fig. 7]. La résolution en surface est ici de l'ordre de 30 à 200 Å suivant les conditions expérimentales choisies.

C - Microanalyse par rétrodiffusion coulombienne

Quand un échantillon est bombardé par des particules chargées de masse m et d'énergie E_0 , l'énergie E des particules rétrodiffusées à 180° par un noyau de masse M est donné par la relation :

$$E = E_0 \left[\frac{M - m}{M + m} \right]^2$$

Le spectre en énergie des particules rétrodiffusées dépend donc des diverses masses des noyaux présents dans la cible. Cette méthode est particulièrement bien adaptée pour la microanalyse d'éléments lourds sur des substrats légers. De plus dans ce cas on obtient une forte sensibilité car la section efficace coulombienne croît comme le carré du numéro atomique du noyau. Des faisceaux d' He^4 ou de C^{12} sont généralement utilisés pour de telles expériences.

II Application de la microanalyse nucléaire à l'étude de l'oxydation anodique de l'aluminium [2] du tantale [3] et du silicium [4]

Il convient de distinguer ici deux cas suivant que l'on utilise ou non des techniques de marquage à l'O¹⁸.

A - Sans marquage à l'O¹⁸

Tous les échantillons examinés seront donc ici de composition isotopique naturelle. Pour les éléments ayant plusieurs isotopes, la microanalyse nucléaire donne la quantité de l'isotope ayant la plus forte abondance naturelle : C¹² pour le carbone (98,89 %), N¹⁴ pour l'azote (99,63 %) et O¹⁶ pour l'oxygène (99,76 %).

- 1° Mesure d'épaisseurs équivalentes

On peut définir, pour des films minces et homogènes de composition chimique connue, une épaisseur géométrique équivalente X à partir de la valeur q du nombre de noyaux par cm² de l'un des constituants du film. Cela implique la connaissance, d'une part de la stœchiométrie et de la densité du composé chimique considéré, d'autre part, du coefficient de rugosité de la surface du substrat. On peut alors écrire :

$$X = \lambda q$$

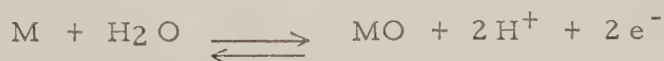
ou λ est une constante. Néanmoins, dans de nombreux cas, la seule connaissance de la valeur de q suffit pour l'étude de certains phénomènes.

a) Lois de croissance des films d'oxyde anodique

Les figures 1, 2 et 3 de la référence 2 montrent les résultats obtenus respectivement sur du tantale poli, de l'aluminium non poli et de l'aluminium poli, reliant le nombre q_O d'atomes d'oxygène par cm² au potentiel V_{Ox} de l'anode pour diverses densités de courant final. Au cours de l'oxydation anodique, ce potentiel V_{Ox} satisfait la relation :

$$V_{Ox} - V_{eq} = \eta_m + \eta_s + \eta_{Ox}$$

où η_m est la surtension à l'interface métal-oxyde, η_s à l'interface oxyde-solution et η_{0x} à l'intérieur de l'oxyde. V_{eq} est le potentiel d'équilibre de l'anode qui est égal au potentiel thermodynamique V_m de formation de l'oxyde dont la réaction globale peut s'écrire :



où M représente le métal.

Si tout l'oxygène présent à la surface de l'échantillon est contenu dans le film fortement isolant qui se comporte comme une couche d'arrêt, on peut écrire :

$$\eta_{0x} = \lambda E_{0x} q_O$$

où E_{0x} est le champ électrique de formation de l'oxyde. Si le film contient une région de forte conductivité ionique dont le contenu en oxygène est q_O^c , nous avons alors :

$$\eta_{0x} = \lambda E_{0x} (q_O - q_O^c)$$

Il apparaît donc que lorsqu'une couche à forte conductivité ionique est présente sur la surface de l'échantillon, la courbe $q_O = f(V_{0x})$ est translatée vers les potentiels négatifs. De plus si q_O^c est nul, les courbes $q_O = f(V_{0x})$ obtenues pour différentes densités de courant J (donc pour différents champs E_{0x}) coupent l'axe des potentiels au potentiel $V_{0x}(0) = \eta_m + \eta_s$. Les tableaux I et II (2) donnent respectivement les valeurs de $V_{0x}(0)$ et les valeurs du champ E_{0x} de formation pour diverses densités de courant obtenues à partir des lois de croissance $q_O = f(V_{0x})$. De ces résultats, on peut tirer les conclusions suivantes :

- La somme des surtensions $\eta_m + \eta_s$ est pratiquement nulle .
- Le champ E_{0x} est relié à J par une relation de type logarithmique.
- L'aluminium poli électrochimiquement présente en surface une couche initiale de forte conductivité ionique qui donne lieu à une

translation de la loi de croissance $q_O = f(V_{Ox})$ vers les potentiels négatifs.

b) Vitesse de dissolution

La vitesse de dissolution chimique d'un film anodique dans une solution corrosive peut être considérée comme une caractérisation de l'oxyde anodique formé. C'est ainsi que l'on observe [3] une vitesse de dissolution (dans un mélange $NH_4F - HF$) huit fois plus grande pour un "oxyde" de tantale formé dans de l'acide sulfurique concentré (95 %) que pour un oxyde de tantale formé dans une solution aqueuse neutre. Cet effet peut être utilisé pour étudier les mécanismes de croissance de couches "dupleix".

- 2° Détermination du rendement faradique de l'oxydation

La densité de courant J passant à travers l'oxyde peut être décomposée en :

$$J = J_i + J_e$$

où J_i et J_e sont respectivement les densités de courant ionique et électronique. La densité de courant ionique peut, à son tour, se décomposer en :

$$J_i = J_{Ox} + J_{dis}$$

où J_{Ox} est la partie du courant qui contribue à la croissance du film et J_{dis} le courant de dissolution. Nous pouvons estimer la valeur de J_e [3] par l'emploi de système Redox dans la solution. La microanalyse nucléaire permet de déterminer J_{Ox} suivant la relation :

$$q_O(t) - q_O(0) = k \int_0^t J_{Ox}(\theta) d\theta$$

où la constante k vaut $0,312 \cdot 10^{19}$ atomes d'oxygène par coulomb si l'on suppose que l'oxygène est fixé dans le film sous la forme O^{2-} . La mesure précise du nombre Q de coulombs par cm^2

$$Q = \int_0^t J(\theta) d\theta$$

consommée au cours de la croissance anodique permet de déterminer le

rendement faradique de l'oxydation suivant la relation :

$$R = \frac{J_{Ox}}{J} = \frac{1}{k} \frac{dq_0}{dQ}$$

La figure 6 de la référence 2 montre la courbe reliant le nombre q_0 d'atomes d'oxygène déposés au cours de la croissance anodique de l'oxyde d'aluminium (la soustraction du contenu de la couche initiale étant faite) au nombre de coulombs par cm^2 consommés (exprimés en nombre d' O^{--} par cm^2). La pente de cette courbe donne par définition la valeur de R . Les mesures faites en système Redox montrent que la composante électronique J_e du courant n'excède pas 2 % et 5 % du courant total respectivement sur l'aluminium poli et l'aluminium non poli. On peut alors estimer par différence la valeur minimum de la densité de courant ionique J_i (tableau IV, réf. 2). Il ressort de ces résultats que le rendement faradique de l'oxydation sur l'aluminium poli est indépendant de la densité de courant de formation. Pour l'aluminium non poli, la diminution du rendement faradique lorsque le film croît correspond à une augmentation du courant de dissolution puisque la densité de courant électronique reste inférieure à 5 % de la densité de courant total. De plus nous avons prouvé que le fort courant de dissolution observé sur l'aluminium non poli est de nature purement électrochimique. En effet en l'absence de champ la vitesse de dissolution chimique de l'oxyde dans l'électrolyte est estimée à $0,3 \mu A/cm^2$ aussi bien pour l'aluminium poli que pour l'aluminium non poli.

- 3° Stœchiométrie et incorporations

Dans les cas précédents, on supposait la stœchiométrie du film étudié parfaitement connue. Si l'on peut doser chacun des constituants du film, la stœchiométrie du film peut être alors déterminée avec une grande précision (celle des cibles de référence). Lorsque le substrat contient un élément qui entre dans la composition du film (comme l'oxyde d'aluminium sur l'aluminium, etc.), une telle mesure directe n'est pas possible. Néanmoins pour des films d'épaisseur suffisante (de $500 \text{ \AA}$ à $5000 \text{ \AA}$ suivant la nature du film), l'analyse du spectre obtenu par réaction nucléaire ou rétro-

diffusion coulombienne ou de la courbe d'excitation au voisinage d'une résonance, permet de déterminer la stœchiométrie de film composé de deux ou même de trois constituants (1). La figure 8 de la référence 1 montre la courbe d'excitation de la réaction $Al^{27}(p, \gamma) Si^{28}$ observée sur un film d'oxyde d'aluminium au voisinage d'une résonance 992 KeV de la réaction nucléaire. Le rapport des hauteurs (voir annexe) des plateaux montre que le film est bien de la forme $Al_2 O_3$.

Quand l'oxydation anodique est effectuée dans une solution d'acide concentré, on observe [3] de fortes incorporations anions dans le film de sorte qu'il est préférable, dans ce cas, de parler de films d'"oxysels" plutôt que de films d'oxydes. La figure 7 de la référence 3 montre l'incorporation d'azote dans un film anodique formé sur du tantale dans de l'acide nitrique à 93 % en fonction de la teneur en oxygène du film. La pente de la droite donne un taux d'incorporation de $8,8 \pm 0,9$ atomes d'azote pour 100 atomes d'oxygène. L'erreur mentionnée provient essentiellement de la cible de référence utilisée.

- 4° Détermination du rendement en oxygène et des mécanismes d'incorporation [3]

Lorsque le taux d'incorporation d'anions est grand, on peut définir le rendement en oxygène R_O de la formation du film défini par :

$$R_O = \frac{q'_O}{q_O^Q}$$

où q_O^Q est le nombre d'atomes d'oxygène par cm^2 déduit de la densité de charge consommée Q . On suppose, pour déterminer q_O^Q , d'une part que le courant électrique et le courant de dissolution sont négligeables, d'autre part que l'oxygène est incorporé dans le film sous la forme d'ion divalent O^{2-} . q'_O est le nombre réel d'atomes d'oxygène fixé au cours du traitement anodique. Ainsi une valeur de R_O supérieure à l'unité implique une charge moyenne par oxygène inférieure à deux. Ceci ne peut s'expliquer que par une incorporation d'anions polyatomiques où la charge par atome d'oxygène est inférieure à deux. Par exemple dans NO_3^- , la charge par atome d'oxy-

gène est $\frac{1}{3}$. On voit donc que, en faisant des hypothèses sur la nature des anions incorporés, on peut déduire de la valeur de R_O la fraction des oxygènes incorporée sous forme d'anions polyatomiques. Le tableau 3 de la référence 3 donne les valeurs du rendement en oxygène R_O pour l'oxydation du tantale dans divers électrolytes. Le tableau 4 de cette même référence donne la proportion d'anions polyatomiques par rapport au nombre total d'anions déduite des valeurs de R_O .

Dans le cas du tantale oxydé dans HNO_3 à 93 %, on obtient pour R_O la valeur de 131 %. Les résultats confirment parfaitement l'hypothèse d'incorporation d'anions du type NO_3^- ; en effet le nombre d'atomes d'azote déterminé directement par microanalyse nucléaire $((7,7 \pm 0,8) \times 10^{14}$ atomes/cm²/volt) est très proche de celui déduit de la valeur de R_O ($7,4 \times 10^{14}$ atomes/cm²/volt).

B - Marquage à l'O¹⁸

La microanalyse nucléaire permet d'effectuer des expériences de marquage au C¹³, N¹⁵, ou O¹⁸. Le marquage à l'O¹⁸ est particulièrement bien adapté à l'étude de l'oxydation anodique. Il est aisé d'obtenir des produits (H₂O, acide citrique, KNO₃, etc) fortement enrichis en O¹⁸ (jusqu'à 95 % comparé au 0,204 % de concentration isotopique naturelle) en provenance de l'Institut Weizmann en Israël. De plus il peut être fort utile dans certains cas d'utiliser de l'eau appauvrie en O¹⁸ (jusqu'à 0,007 % en O¹⁸). La concentration isotopique C en O¹⁸ d'un film d'oxyde est déterminé par :

$$C = \frac{q_{O^{18}}}{q_{O^{18}} + q_{O^{16}}}$$

où $q_{O^{18}}$ est mesuré par la réaction $O^{18}(p, \alpha)N^{15}$ et $q_{O^{16}}$ par la réaction $O^{16}(d, p)O^{17*}$. En raison de la forte sensibilité du dosage de l'O¹⁸, on peut déterminer des concentrations isotopiques allant jusqu'à 10⁻⁵

- 1° Les sources de l'oxygène [3,4]

Quand un électrolyte contient plusieurs composés oxygénés, on peut déterminer par des expériences de marquage à l'O¹⁸ la source de l'oxygène présent dans le film d'oxyde. Pour ce faire, il importe de prouver

auparavant qu'il n'y a pas d'échange isotopique d'oxygène entre les composants de l'électrolyte. Si l'un des composants de l'électrolyte est marqué en O^{18} à une concentration isotopique C_0 et si la microanalyse nucléaire donne pour l'oxyde formé une concentration isotopique C , la concentration normalisée :

$$C^* = \frac{C}{C_0}$$

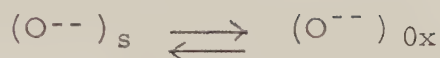
donne directement la contribution en oxygène du composé marqué pour la croissance du film d'oxyde.

Nous avons effectué de telles expériences [4] pour l'étude des sources de l'oxygène dans des solutions de N - méthylacétamide (N M A) et de glycol, contenant 0,4 % de KNO_3 et de 0,1 à 1 % d'eau lors de l'oxydation anodique du silicium et du tantale. Par le marquage de l'eau ou du KNO_3 , nous avons montré que la principale source d'oxygène est l'eau ; le bain organique ne contribue pas directement à cette source ; en effet nous avons montré que le passage du courant provoque l'apparition d'eau au voisinage de l'anode en quantité proportionnelle au nombre de coulombs passés, l'oxygène de cette eau provenant du solvant organique. Cette eau, se mélangeant à l'eau déjà présente, conduit à une dilution isotopique progressive. Cependant la concentration absolue de l'eau par rapport au solvant n'a aucune influence sur la composition isotopique des couches ; ce qui prouve bien que le solvant ne fournit des oxygènes aux couches d'oxyde que de façon indirecte. La contribution du sel (de l'ordre de 10 %) décroît quand la concentration d'eau par rapport au sel dans le bain croît. Ceci est illustré par la figure 6 de la référence 4 qui montre que $1/C^*$ varie linéairement avec la proportion d'eau aussi bien pour le tantale que pour le silicium. De plus nous avons montré que le nitrate agit comme fournisseur direct d'oxygène sans incorporation anionique ; en effet, nous avons observé l'absence d'azote dans les films au moyen de la microanalyse nucléaire.

- 2° Echange isotopique d'oxygène

L'échange isotopique d' O^{18} entre un oxyde et la solution est contrôlé par la vitesse de la réaction réversible de transfert à l'interface

oxyde-solution :



où les indices s et ox désignent respectivement la solution et l'oxyde. Pour étudier l'échange isotopique de l'oxygène, on plonge un oxyde, initialement formé dans une solution appauvrie en O^{18} , dans une solution chimiquement identique et fortement enrichie en O^{18} et l'on détermine par la microanalyse nucléaire l'accroissement du nombre d'atomes d' O^{18} dans l'oxyde en fonction du temps d'échange. Dans cette expérience, il importe qu'il n'y ait aucune croissance et aucune dissolution de l'oxyde. Le courant d'échange J_{ex} caractérise cette réaction de transfert. Le flux net $J_{O^{18}}$ d'atomes d' O^{18} entrant dans l'oxyde est après un temps t :

$$J_{O^{18}} = J_{ex} \left[C_s^o(t) - C_{ox}^o(t) \right]$$

où $C_s^o(t)$ est la concentration isotopique en O^{18} à l'interface. On admet généralement que $C_s^o(t)$ est constant et égal à la concentration isotopique de la solution C_s . L'accroissement du nombre d'atomes d' O^{18} $q_{O^{18}}(t)$ dépend de plus du coefficient d'autodiffusion D de l'oxygène dans l'oxyde. On démontre que J_{ex} est égal à la pente de la courbe $q_{O^{18}}^*(t) = q_{O^{18}}(t)/C_s$ au temps $t = 0$ et D est proportionnel à la pente de la courbe $q_{O^{18}}$ en fonction de $\sqrt{t}$ aux temps longs.

La figure 7 de la référence 2 montre l'échange isotopique d'un oxyde de tantale et d'un oxyde d'aluminium initialement formés dans une solution appauvrie en O^{18} (0,007 % O^{18}) puis plongés dans une solution identique enrichie à 80 % en O^{18} . L'effet de saturation observé pour le tantale montre que le coefficient D est négligeable et que l'échange se produit sur les premières couches moléculaires de l'oxyde. On obtient pour J_{ex} les valeurs $0,3 \mu A/cm^2$ et $3 \mu A/cm^2$ respectivement sur l'oxyde de tantale et l'oxyde d'aluminium. Par ailleurs nous avons montré que cet échange est parfaitement réversible en constatant la diminution d' O^{18} lorsque l'échantillon est à nouveau plongé dans une solution de concentration isotopique naturelle.

- 3 ° Mécanisme de transport de l'oxygène au cours de la croissance de film d'oxyde.

L'étude du mécanisme de croissance de la couche d'oxyde anodique consiste à déterminer en premier lieu l'espèce migrante (métal ou oxygène ou bien les deux à la fois) et en second lieu le mécanisme de transport de l'espèce migrante (du type interstitiel ou lacunaire ou bien une combinaison des deux). Dans le mécanisme de transport interstitiel l'ordre initial des atomes est inversé alors que dans le mécanisme de transport lacunaire l'ordre est conservé. Dans ce dernier type de transport on peut observer un certain mélange des atomes dont l'importance dépend du degré de corrélation du transport lacunaire.

Le marquage à l' O^{18} permet d'étudier le mécanisme de transport de l'oxygène au cours de la croissance du film d'oxyde. L'expérience consiste à former tout d'abord un oxyde dans un électrolyte enrichi en O^{18} puis à poursuivre l'oxydation dans un électrolyte identique de concentration isotopique naturelle ou appauvrie en O^{18} (dans certains cas il peut être préférable de choisir l'ordre inverse). On compare alors la teneur en O^{18} du "sandwich" $O^{18} - O^{16}$ à celle d'un oxyde ayant seulement subi le traitement dans l' O^{18} ; ceci permet de vérifier si la quantité d' O^{18} reste conservée lors du traitement dans l'électrolyte non marqué. En localisant les noyaux d' O^{18} dans le "sandwich", on peut déterminer si l'ordre des oxygènes est conservé. Ceci est obtenu par l'analyse de la courbe d'excitation au voisinage d'une résonance fine de la réaction nucléaire $O^{18}(p, \alpha) N^{15}$ (voir annexe). En effet si l'ordre des atomes d'oxygène reste conservé, la couche contenant l' O^{16} est en surface et l'on observe alors la résonance de la réaction $O^{18}(p, \alpha) N^{15}$ à une énergie supérieure à l'énergie de résonance de telle sorte que la différence d'énergie observée corresponde à la perte moyenne d'énergie du faisceau incident dans la couche contenant l' O^{16} . Les calculs développés en annexe permettent de déterminer le profil $C(x)$ des noyaux O^{18} dans le "sandwich" considéré. Dans certains cas on peut aussi obtenir le profil $C(x)$ de l' O^{18} par la mesure de la teneur en O^{18} du "sandwich" après des attaques chimiques successives de l'oxyde.

La figure 7 de la référence 1 montre un résultat typique obtenu

sur le tantale ; la figure 7a représente la courbe d'excitation de la réaction $O^{18}(p, \alpha) N^{15}$ au voisinage de la résonance à 629 KeV obtenue sur un film mince (70 Å : correspondant à une perte moyenne d'énergie du faisceau de 650 eV) enrichie à 80 % en O^{18} . La figure 7b montre la courbe d'excitation obtenue dans les mêmes conditions sur un "sandwich" qui a été oxydé jusqu'à 30 V dans une eau enrichie en O^{18} à 80 % puis jusqu'à 90 V dans une eau naturelle et enfin de nouveau jusqu'à 100 V dans une eau enrichie en O^{18} . Les deux pics parfaitement séparés montrent clairement que l'ordre des oxygènes reste conservé et le "sandwich" correspond (de la surface vers le métal) à $140 \text{ Å } O^{18} + 840 \text{ Å } O^{16} + 520 \text{ Å } O^{18}$. La résolution en profondeur obtenue en surface est de l'ordre de 200 Å dans Ta_2O_5 .

La figure 19 de la référence 1 montre la courbe d'excitation obtenue au voisinage d'une résonance très fine ($\Gamma < 100 \text{ eV}$) de la réaction $O^{18}(p, \alpha) N^{15}$ à 1165 KeV. La cible est constituée d'un film d' Al_2O_3 oxydé jusqu'à 20 V dans une solution enrichie à 80 % en O^{18} puis jusqu'à 55 V dans une solution naturelle et jusqu'à 60 V dans une solution enrichie en O^{18} (croissance de 12 Å/V dans les conditions expérimentales). Le pic très étroit à gauche (650 eV à mi hauteur) montre que l'oxygène de la dernière oxydation en O^{18} est en surface. En effet, la perte moyenne d'énergie dans un film formé à 5 V (60 Å) est de 350 eV ; la dispersion en énergie du faisceau est de 250 eV. On voit donc ici que, comme pour le tantale, l'ordre des atomes d'oxygène est conservé ; de plus le pic de droite élargi suggère qu'il y aurait un certain mélange des atomes d'oxygène 16 et 18 .

L'interprétation théorique de telles courbes d'excitation fait l'objet de calculs exposés dans l'annexe. Ces calculs font appel à la théorie stochastique de l'interaction des particules avec la matière. La détermination théorique du profil $C(x)$ à partir de la courbe d'excitation a pu être appliquée à d'autres problèmes (diffusion d' O^{18} dans ZrO_2 et dans Zr , localisation de trace de fluor dans l'oxyde de tantale, etc). La mise au point complète de cette méthode permettra d'étendre ces mesures à des études de phénomènes de transport à des systèmes plus complexes tels que les films d'oxysels obtenus lors de l'oxydation du tantale dans des bains d'acide concentré ou les oxydes anodiques obtenus sur les nitrures de silicium ou de tantale.

Conclusion

La microanalyse des isotopes 16 et 18 de l'oxygène par l'observation directe de réactions nucléaires est particulièrement bien adaptée à l'étude de l'oxydation anodique. Cette méthode peut s'étendre à d'autres noyaux légers comme Cl^{35} et N^{15} pour des études de marquage. De plus le domaine d'application de la microanalyse nucléaire est vaste. Ceci est illustré par les nombreuses expériences utilisant ces techniques qui ont été exécutées dans le laboratoire comme en particulier les applications en métallurgie (phénomène de ségrégation, diffusion d'oxygène dans les métaux, autodiffusion dans les oxydes), en électrochimie (corrosion, passivité, catalyse) et en biologie (phénomène de transport de l'eau à travers le système vasculaire et pulmonaire ; échange d'oxygène du cerveau avec le milieu extérieur). En ce qui concerne l'oxydation anodique, cette méthode a permis d'acquérir des connaissances précises sur les lois de croissance de ces oxydes, la valeur de la surtension à l'interface oxyde-solution, le rendement faradique de l'oxydation, le taux d'incorporations d'anions polyatomiques, les sources de l'oxygène, l'échange isotopique de l'oxygène entre l'oxyde et la solution et enfin sur le transport de l'oxygène au cours de la croissance du film.

*Part II. Applications to materials analysis 481-515***MICROANALYSIS BY THE DIRECT OBSERVATION OF NUCLEAR REACTIONS
USING A 2 MeV VAN DE GRAAFF***

G. AMSEL, J. P. NADAI, E. D'ARTEMARE, D. DAVID, E. GIRARD and J. MOULIN

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Tour 23; 9, quai Saint-Bernard, Paris 5e, France

The principles of nuclear microanalysis by the direct observation of the charged particles emitted from nuclear reactions induced on light nuclei are described. This method allows the determination, in short times, of very small quantities of nuclei like ^{16}O , ^{18}O , ^{14}N , ^{19}F , etc. near the surface of samples. Typical sensitivities are of the order of 10^{14} atom/cm². Concentration profiles as a function of depth may be directly measured with submicron

resolution. The technical details of a facility comprising a 2 MeV Van de Graaff accelerator are given. Problems related to particle detection and data recording are discussed. The various scattering chambers, which allow most of the measurements to be carried out automatically with digital control, are described. Applications to various fields in solid state physics, metallurgy and electrochemistry are presented.

1. Introduction

The study of physical and chemical phenomena taking place near the surface of solids requires quantitative determination and localization in depth of very small amounts of elements. Such studies are fundamental in solid state physics (diffusion phenomena, growth mechanisms of thin films, trace contamination of surfaces, ion implantation, etc.), in metallurgy (corrosion phenomena, surface impurities, etc.), in electrochemistry (passivity of metals, electrode behaviour, ion transport in catalysis, etc.), and in other fields where surface reactions are of interest. Tracer experiments with separated isotopes may give further insight in such phenomena as atomic transport, self-diffusion and surface exchange with external media. Conventional analytical techniques do not always allow such measurements, especially when high sensitivity as well as good depth resolution are required. The radioactive isotopes of light elements like oxygen and nitrogen are too short-lived to allow most of the tracer experiments to be carried out. The electron probe integrates information over about the first micron of the sample, has low sensitivity for light elements and cannot distinguish between isotopes. The ion probe is generally effective only for depths above about 100 Å owing to transient phenomena at the start of the ion bombardment. The ionization yield of the sputtered atoms varies strongly with the chemical composition of the sample; hence quantitative measurements are possible only in special instances¹). Infrared and NMR techniques may be applied only in particular cases. The relative merits, for the study of surface phenomena, of conventional techniques with respect to those presented here are discussed in more detail elsewhere^{2,3}).

Nuclear techniques provide an alternative for the determination of small amounts of nuclei. Activation analysis by neutrons and γ -rays^{4,5}) or by charged particles⁶⁻⁹) may be used with advantage in many experiments, especially to measure trace impurities in the bulk of the samples. On the other hand, the direct observation of nuclear reactions induced by charged particles has specific advantages for measurements near the surface of substrates, which were stressed in refs. 2 and 3 and will be illustrated below. Many of the theoretical and physical aspects of this method and of its applications to various fields were described in several papers devoted to the microanalysis of nitrogen and of the stable isotopes of oxygen^{2,3,10-14}).

The aim of this paper is to describe briefly this analytical method emphasizing the technical details necessary for its efficient application. We shall show how a small Van de Graaff accelerator may be used as a general purpose facility for nuclear microanalysis. Considering the large number of low energy accelerator facilities which exist nowadays, it is hoped that nuclear microanalysis will be widely used in the near future.

2. Principles**2.1. GENERAL**

Charged particles in the 0.5 to 2 MeV energy range are accelerated to induce nuclear reactions on low Z nuclei. For medium and high Z nuclei elastic scattering may be observed. The emitted charged particles are detected by means of semiconductor detectors and their energy spectrum is recorded; the interpretation of these spectra allows identification of the nuclei in the target. This microanalytical procedure has the following properties:

- The analysis is restricted to the first microns of the sample.

* Supported by the Centre National de la Recherche Scientifique (RCP N° 157), the D.G.R.S.T. and the D.R.M.E.

- There is no natural background.
- High positive Q values are frequently encountered (see table 1), and low-energy particles may lead to high yields for low Z nuclei. This has the advantage of reduced local heating of the target, and of requiring only small accelerators.
- Medium and high Z nuclei practically do not contribute to nuclear reactions, owing to Coulomb barrier repulsion at low energies; this allows traces of low Z nuclei to be detected in heavier substrates. Elastically scattered particles may easily be stopped, using suitable absorbers, generally mylar, which is pinhole-free.
- Nuclear reactions are specific: well defined energy groups characteristic of the nuclei are observed; two isotopes of the same element behave quite differently. In many cases, only one of the isotopes has a positive Q value, the other being ignored whatever its concentration. For elastic scattering the situation is less favourable; the outgoing energy E at backward angles being:

$$E = E_0 \left[\frac{M - m}{M + m} \right]^2 \quad (1)$$

(where E_0 is the bombarding energy, M the mass of the nucleus and m that of the particle), only low Z isotopes may be distinguished. This method is, however, of great interest when observing traces of high Z elements in a low Z matrix; the yield being enhanced in proportion of Z^2 , a high sensitivity results in this case.

– The results are generally independent of the matrix in which the observed nucleus is embedded as the reaction yield depends only on nuclear cross sections: the physical or chemical states of the nuclei in the matrix have no influence, provided the sample remains stable under vacuum and particle bombardment. The only exceptions to this rule are channeling effects in precisely oriented single crystals (see below).

– The results are quantitative, a 1% precision being easily reached.

– The method is nondestructive.

– The sensitivity may be very high; down to some 10^{-12} g of matter may be determined in favourable cases.

– The measurements are very quick; most of the results are obtained within some minutes.

– Samples at high temperature and under relatively high gas pressures (up to some tens of microns of Hg) may be examined if necessary.

– Depth distributions may be determined in the first microns with a resolution of the order of 0.1 μm

and using special techniques, of 50 to 100 Å near the surface.

On the other hand the lateral resolution is poor; of the order of 0.1 mm for very well collimated beams. Hence only reasonably uniform samples may be examined, in contrast with the electron and ion probes. Thus these methods are fully complementary.

The bombarding particles used are mainly protons and deuterons, ^4He or ^{12}C being useful for elastic scattering, to increase mass resolution [see eq. (1)]. Reactions induced by ^3He and ^4He are not considered here, as they require generally rather high bombarding energies. Tritons require specially equipped accelerators and will not be considered.

Usually charged particles are detected: protons, deuterons (elastic scattering), α -particles, etc. This choice is motivated by the existence nowadays of high performance semiconductor detectors. γ -rays, detected by NaI(Tl) scintillation counters, are used when narrow strong resonances show up in the cross section curves like for $^{27}\text{Al}(\text{p},\gamma)^{28}\text{Si}$ at 992 keV, or for $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$; these resonances restore the specificity of the method, lost due to the complicated character of γ -ray spectra. In some cases γ -ray detection with Ge(Li) semiconductor detectors may be useful, but the detection efficiency is usually lower than for charged particles. Neutrons may be detected in some cases, especially near thresholds like for $^7\text{Li}(\text{p},\text{n})^6\text{He}$ at 1881 keV. The energy analysis of fast neutrons requires sophisticated equipment, involves low solid angles and does not generally present marked advantages with respect to charged particles, except for some favourable cases. Table 1 lists the Q values of (p, α), (d, α) and (d,p) reactions for light nuclei, in decreasing order; it gives an idea of the nuclei which may be determined by these methods and of the interferences which may arise when several light nuclei are simultaneously present in the sample.

Microanalysis by nuclear reactions was first used in 1962¹⁵) and was applied to the study, by ^{18}O tracing, of oxygen transport in anodic aluminium oxide. Ollerhead et al.¹⁶) used $^{17}\text{O}(^3\text{He}, ^4\text{He})^{16}\text{O}$ to study oxide layers; Moeller and Starfelt¹⁷) investigated fluorine contamination by $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$. Sabine et al.¹⁸) used highly collimated proton beams inducing (p, α) and (p, γ) reactions for lateral distribution measurement. Recently, Quaglia et al.¹⁹) applied nuclear reaction techniques to ^{16}O , ^{12}C and Ligeon et al.²⁰) to ^{11}B . Moeller et al.²¹) and Naude et al.²²) used (d,n) reactions to detect ^{16}O , ^{14}N and ^{12}C .

Elastic scattering was used as early as 1959 by Rubin²³) for surface analysis. With the same method

TABLE I

Q values for nuclear reactions induced by protons and deuterons on some light isotopes.

Isotope	Q_0 (MeV)	Isotope	Q_0 (MeV)	Isotope	Q_0 (MeV)
(p, α) reactions:					
^7Li	17.347	^6Li	4.02	^9Be	2.125
^{11}B	8.582	^{18}O	3.970	^{31}P	1.917
^{19}F	8.119	^{37}Cl	3.030	^{27}Al	1.594
^{15}N	4.964	^{23}Na	2.379	^{17}O	1.197
				^{10}B	1.147
(d, α) reactions:					
^{10}B	17.819	^{11}B	8.022	^{32}S	4.890
^6Li	22.36	^{15}N	7.683	^{18}O	4.237
^7Li	14.163	^9Be	7.152	^{30}Si	3.121
$^{14}\text{N}_{(\alpha_0)}$	13.579	^{25}Mg	7.047	^{16}O	3.116
^{19}F	10.038	^{23}Na	6.909	^{26}Mg	2.909
^{17}O	9.812	^{27}Al	6.701	^{24}Mg	1.964
$^{14}\text{N}_{(\alpha_1)}$	9.146	^{29}Si	6.012	^{28}Si	1.421
^{31}P	8.170	^{13}C	5.167	^{12}C	< 0
(d,p) reactions:					
^{10}B	9.237	^{17}O	5.842	^{26}Mg	4.212
^{25}Mg	8.873	^{27}Al	5.499	^{12}C	2.719
$^{14}\text{N}_{(\text{p}_0)}$	8.615	^{24}Mg	5.106	^{16}O	1.919
^{29}Si	8.390	^6Li	5.027	^{18}O	1.731
^{32}S	6.418	^{23}Na	4.734	$^{14}\text{N}_{(\text{p}_s)}$	1.305
^{28}Si	6.253	^9Be	4.585	^{11}B	1.138
^{13}C	5.947	^{19}F	4.379	^{15}N	0.267
^{31}P	5.712	^{30}Si	4.367	^7Li	< 0

Edge and Lankford²⁴) studied irregular surfaces, Pierce et al.²⁵) lateral distributions and Turos and Wilhelmi²⁶) thickness measurements and chemical analysis. Elastic scattering was widely used in recent years for the study of channeling phenomena.

It is worth noting the interesting work of Hart et al.²⁷) who detected proton induced characteristic X-rays to identify light nuclei. This method may in some cases supplement nuclear reactions, as it requires very low energies, in the 100 keV range; it is, however, nearer to the electron probe than to nuclear methods.

2.2. THE MEASUREMENT OF THE TOTAL AMOUNT OF NUCLEI IN SURFACE REGIONS

Let us suppose that the bombarding energy E_0 is in the vicinity of a plateau of the differential cross section curve $\sigma_\theta(E_0)$, i.e. that for a given ΔE_0 , $\sigma_\theta(E) \approx \sigma_\theta(E_0)$ for $E_0 - \Delta E_0 < E < E_0$. Then at depths x of the target where the beam energy loss is less than ΔE_0 , say $x < x_0$, σ_θ appears as constant and if the nuclei to be determined are all contained in the surface region $x < x_0$ the counting rate $N(E_0)$ will be:

$$N(E_0) = ki\sigma_\theta(E_0)\Omega \int_0^{x_0} C(x)dx, \quad (2)$$

where k is a constant, i is the beam current, $\sigma_\theta(E_0)$ the differential cross section in the direction of observation θ and Ω the solid angle of detection (the detection efficiency being 1 for semiconductor detectors). The quantity

$$q = \int_0^{x_0} C(x)dx \quad (3)$$

is the *total amount* of nuclei in the surface region of the sample, $C(x)$ being the number of nuclei per cm^3 at depth x ; q is expressed in atom/cm^2 , or in other units like mg/cm^2 . For thin films of known composition and density, $N(E_0)$ is thus proportional to the film thickness which may be given in Ångström units. Absolute quantities q may be obtained by comparison to reference standards (see below), and the results are independent of the shape of the distribution profile $C(x)$, provided $C(x) = 0$ for $x > x_0$. If there is no real plateau in the cross section curve a slight correction²⁾ still usually allows quantitative determination of nuclei up to depths x_0 of about 1 μm .

Usually the detection is at backward angles (150° to 165°). The nuclei routinely determined in this way in our laboratory (for Q values see table 1) are $^2\text{H}[\text{D}(\text{d},\text{p})\text{T}]$; $^6\text{Li}[^6\text{Li}(\text{d},\alpha)^4\text{He}]$; $^7\text{Li}[^7\text{Li}(\text{p},\alpha)^4\text{He}]$; $^{12}\text{C}[^{12}\text{C}(\text{d},\text{p})^{13}\text{C}]$; $^{14}\text{N}[^{14}\text{N}(\text{d},\alpha)^{12}\text{C}]$ and $^{14}\text{N}(\text{d},\text{p})^{15}\text{N}$; $^{16}\text{O}[^{16}\text{O}(\text{d},\text{p})^{17}\text{O}]$; $^{18}\text{O}[^{18}\text{O}(\text{p},\alpha)^{15}\text{N}]$; $^{19}\text{F}[^{19}\text{F}(\text{p},\alpha)^{16}\text{O}]$; $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ and $^{19}\text{F}(\text{d},\alpha)^{17}\text{O}]$ and $^{27}\text{Al}[^{27}\text{Al}(\text{p},\gamma)^{28}\text{Si}]$. The detection of ^{15}N is being investigated.

Let us illustrate this method by some results; more details may be found in ref. 14 for ^{14}N , refs. 2, 3, 11, for ^{16}O and ^{18}O and ref. 28 for ^6Li , ^7Li and ^{19}F . Fig. 1 shows cross section curves for ^{16}O , ^{18}O and ^{14}N . For ^{16}O a convenient plateau extends from 800 to 900 keV for the $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}$ reaction ($Q_1 = 1.048$ MeV), leading to the first excited state of ^{17}O [more efficient to use than the fundamental level²⁾]. For ^{18}O the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reaction (leading to a single energy group) presents a very high cross section which is reasonably stationary near 730 keV; the $^{16}\text{O}(\text{p},\alpha)^{13}\text{N}$ reaction has a negative Q value and hence there is here no interference with natural oxygen except for the natural abundance of ^{18}O (0.204%). In practice only chlorine and boron may interfere with the analysis of ^{18}O , an exceptionally favourable case for nuclear microanalysis. ^{14}N may be determined by a variety of deuteron induced reactions, those leading to α -particles being the less liable to interfere with other reactions. The reaction $^{14}\text{N}(\text{d},\alpha_1)^{12}\text{C}$ presents an excellent

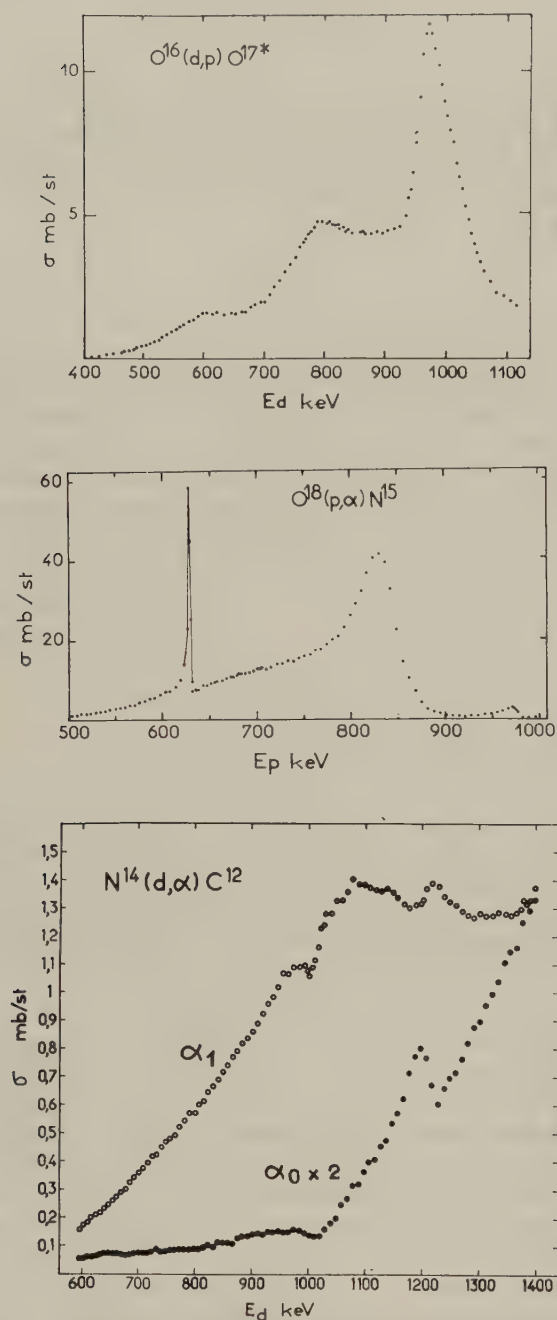


Fig. 1. Differential cross sections of the reactions used to analyse ^{16}O , ^{18}O (at 165°) and ^{14}N (at 150°).

plateau above 1100 keV. The α_0 particle from $^{14}\text{N}(\text{d},\alpha_0)^{12}\text{C}$ is the most energetic which may arise from (d, α) reactions after that from ^{10}B (table 1, taking into account the kinematics at backward angles), and is of great help in some cases, although its cross section is lower than for α_1 .

Fig. 2 shows a typical spectrum of (d,p) reactions on oxygen, exhibiting peaks for ^{16}O and ^{12}C (from carbon contamination of the sample). Let us notice that although many reactions have a higher Q value than $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$, a convenient choice of the bombarding energy may avoid disturbing backgrounds. Thus when measuring ^{16}O on massive aluminium or silicon backings, operation at 830 keV allows measurement of some monolayers of oxide without interference from the substrate. Fig. 3 shows a typical spectrum from a tantalum nitride target bombarded with deuterons. If ^{14}N and ^{16}O are to be measured simultaneously the $^{16}\text{O}(\text{d},\text{p}_0)^{17}\text{O}$ reaction should be used, as seen in this spectrum.

Table 2 gives typical counting rates for nuclear microanalysis, showing the high sensitivity of the method. Let us remark, for illustration, that 10^{16} atoms of oxygen/cm² weigh $0.27 \mu\text{g}/\text{cm}^2$ and are equivalent to a $17.6 \text{ \AA}$ thick Al_2O_3 oxide layer. Thus films much thinner than a monolayer are easily measured with some percent statistical precision, in short times.

2.3. CONCENTRATION PROFILES FROM ENERGY SPECTRA

Much information may be gained on the concentration profile $C(x)$ by analysing the energy spectrum of the detected particles. Fig. 4 shows the geometry of the problem. Let S be the energy loss per unit length for the ingoing particle, and S' that of the outgoing particle. The energy at depth x is $E_M(x)$:

$$E_M(x) = E_0 - yS = E_0 - (xS/\cos \phi) = E_0 - \varepsilon x. \quad (4)$$

Let E' be the energy of the particle produced by the

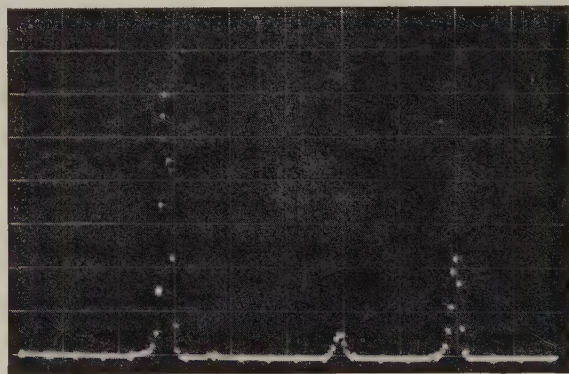


Fig. 2. A typical proton spectrum from the deuteron bombardment of a $800 \text{ \AA}$ thick Ta_2O_5 target on tantalum backing. The p_1 and p_0 peaks of $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$ are seen and the p_0 peak of $^{12}\text{C}(\text{d},\text{p})^{13}\text{C}$ (on the right, from carbon contamination). $E_0 = 830 \text{ keV}$, $19 \mu\text{m}$ mylar; energy of p_1 at detection 950 keV ; 15 keV/channel .

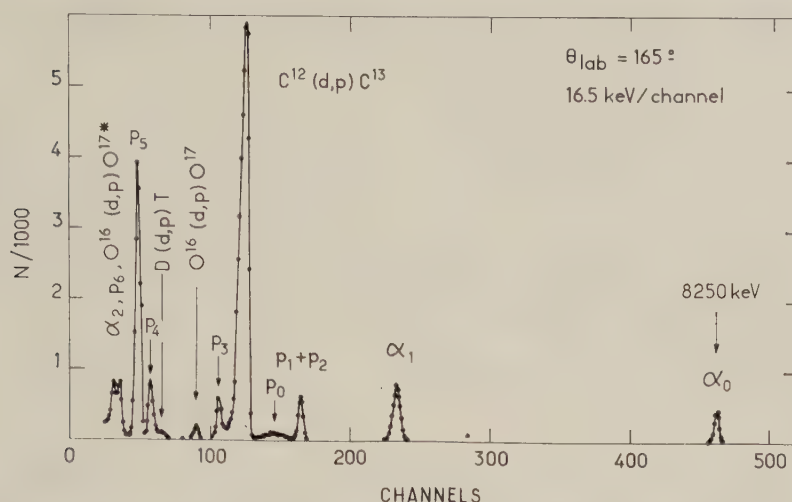


Fig. 3. A typical energy spectrum from the deuteron bombardment of a 1400 Å thick tantalum nitride target on tantalum backing. $E_0 = 1200$ keV, 19 μm mylar.

TABLE 2

Typical experimental conditions for nuclear microanalysis. The counting rates may be multiplied by 3, using three identical detectors, when necessary.

Nucleus	^{16}O	^{18}O	^{14}N	^{19}F	^{12}C	^2H
Reaction	$^{16}\text{O}(\text{d,p})^{17}\text{O}^*$	$^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$	$^{14}\text{N}(\text{d},\alpha)^{12}\text{C}$	$^{19}\text{F}(\text{p},\alpha)^{16}\text{O}$	$^{12}\text{C}(\text{d,p})^{13}\text{C}$	$\text{D}(\text{d,p})\text{T}$
Bombarding energy (keV)	830	730	1300	1340 ^c	1000	550
Energy of emitted particles (MeV)	1.52	3.38	3.76	6.92	7.12 6.92 6.13 } γ	2.45
Thickness of mylar absorber (μm)	19	12	19	31	19	6
Counting rate ^a	1600	4600	470	315	4200 ^b	2000

^a For a film containing 10^{16} atoms/ cm^2 , a 1 μA beam, per minute. The solid angle is 0.12 sterad, at 150° detection angle.

^b 3 in. % 3 in. NaI(Tl) scintillation detector at 7 cm.

^c For films of equivalent thickness < 10 keV.

nuclear reaction for an incident energy E_M . One may write a linear approximation for the kinematics:

$$E' = KE_M + h. \quad (5)$$

Hence

$$E'_M = KE_0 + h - yKS.$$

The energy of the emerging particle, produced at depth x is:

$$E(x) = KE_0 + h - yKS - lS'.$$

Finally:

$$E(0) - E(x) = x \left[\frac{KS}{\cos \phi} + \frac{S'}{|\cos(\theta - \phi)|} \right] = xU. \quad (6)$$

We see that there is a one to one correspondence between the detected energy and the depth, provided energy straggling and finite detector resolution are

neglected. The relative influence on $E(x)$ of the paths of the ingoing and outgoing particles depends on the nature of the reaction, according to the values of

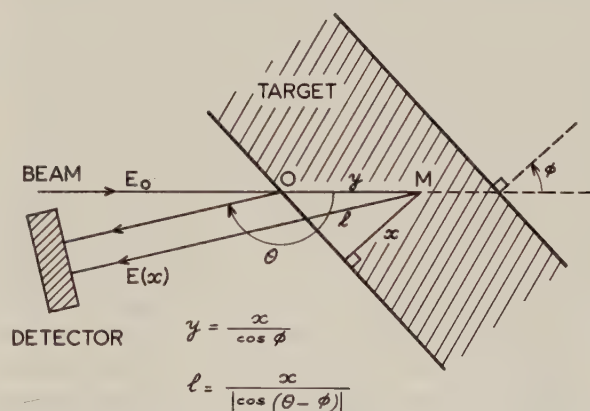


Fig. 4. Geometry of the particle trajectories in the target.

K , S and S' and on the target tilting angle ϕ . By tilting the target, a depth magnification effect is achieved; a well collimated beam and a very flat sample surface is required if one wants $1/\cos \phi$ greater than 2 or 3. If S and S' may not be considered as constant, or the kinematic relation as linear, an empirical relation:

$$E(x) = \Psi(x) \quad (6a)$$

is easily established using the known range-energy relationships in the sample material¹³). In this work we used the data compiled in ref. 29.

The ideal energy spectrum $\mathcal{N}(E)$ of the detected particles is deduced from:

$$\mathcal{N}(E)dE = C(x)dx\sigma_\theta[E_M(x)]ki\Omega.$$

If ΔE is the channel width, the counting rate $\mathcal{N}_i$ in the channel corresponding to the interval $[E_i, E_i + \Delta E]$ is:

$$\mathcal{N}_i = C(x)\sigma_\theta[E_M(x)] \left| \frac{dx}{dE} \right| \Delta E ki\Omega, \quad (7)$$

where x is given from E_i by (6), $E_M(x)$ by (4) and $|dx/dE|$ is deduced from (6). The real spectrum is obtained by taking into account the energy spread effects and the finite energy resolution of the detector. Such detailed calculations were carried out in refs. 3, 11, 12, 13 and 26. Relation (7) allows analysis of the energy spectrum and calculation of $C(x)$ provided $\sigma_\theta(E_0)$ is carefully measured with a very thin target. Here again it is often advantageous to operate with E_0 in the vicinity of a plateau of $\sigma_\theta(E_0)$, but resonances may also be helpful, as shown below.

Fig. 5 shows a typical spectrum corresponding to a thick target for the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction. Curve 2 shows the thin target detector response which determines the depth resolution: target 80 Å thick anodic Ta_2O_5 oxide on tantalum, enriched to 80% ^{18}O ; absorber: 10 µm mylar (which stops protons up to 690 keV); $E_0 = 680$ keV; $\theta = 165^\circ$; $\phi = 0$; beam dose 100 µC; 2 cm² detector at 9.5 cm. The width at half maximum is 68 keV mainly due to energy straggling in the absorber. Curve 1 shows the spectrum for a uniform [$C(x) = \text{constant}$] zirconium dioxide layer (13 µm thick, greater than the range of the protons) labelled to 85% ^{18}O . The depth resolution equivalent to the thin target response width is 0.19 µm in ZrO_2 . This value is typical for this method. The peak at the left in curve 1 is due to the sharp resonance in the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction (see fig. 1b). The general trend of the spectrum on a uniform target is that of the cross section curve below E_0 , as shown by eq. (7) (see fig.

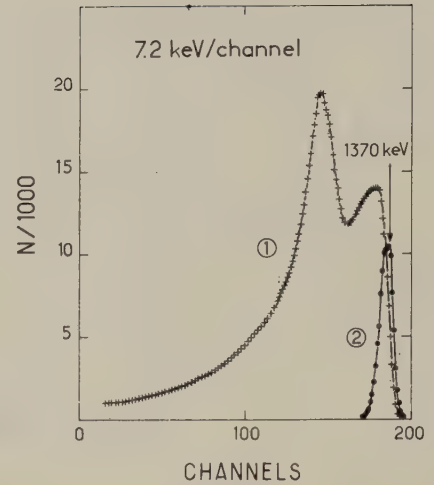


Fig. 5. α particle spectrum from a thick ^{18}O enriched ZrO_2 target (curve 1) for the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction. Curve 2 shows the thin target response. $E_0 = 680$ keV.

1b). Such resonances may be put to benefit as will be shown now.

2.4. CONCENTRATION PROFILES FROM RESONANCES

The depth resolution in the method outlined above is limited by the available energy resolution of the detectors and by energy straggling in the generally unavoidable absorber. Only the use of a high resolution magnetic analyser could overcome this problem; this is generally out of reach, and would lead to great experimental difficulties. In the particular case where there exists a strong narrow resonance in the cross section curve $\sigma_\theta(E_0)$, the measurement of the yield curve $N(E_0)$ of all the emitted particles as a function of the energy E_0 in the vicinity of the resonance energy E_R may give valuable information on the concentration profile $C(x)$. Fig. 6 illustrates this principle: if $E_0 > E_R$ the protons, upon slowing down, reach the energy E_R in the vicinity of a depth x_0 . The yield is hence proportional to $C(x_0)$. $N(E_0)$ is thus an image of $C(x)$. In reality straggling effects rapidly widen the inherently narrow depth resolution of this method, as the real relation between $N(E_0)$ and $C(x)$ is:

$$N(E_0) = \left[\int_0^\infty \int_0^\infty C(x)\sigma_\theta(\eta)W(E_0,\eta,x)dx d\eta \right] \times \text{constant}, \quad (8)$$

where $W(E_0,\eta,x)$ is the probability that a particle of a bombarding energy E_0 (which is the mean value of the beam energy probability distribution) has at the depth x an energy in the vicinity of η . Methods to solve eq. (8) implying the calculation of $W(E_0,\eta,x)$ using the

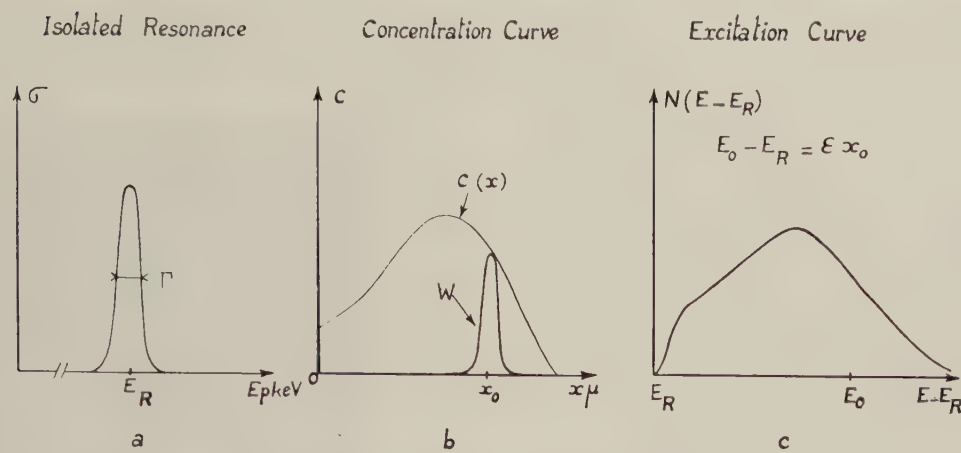


Fig. 6. Principle of concentration profile measurements using narrow resonances.

stochastic theory of the slowing down of particles, are presented in refs. 10 and 11 and will be the subject of a forthcoming paper. However, much qualitative information may be gained from the yield curve $N(E_0)$ without deep mathematical analysis, as shown in ref. 15 and in the following results.

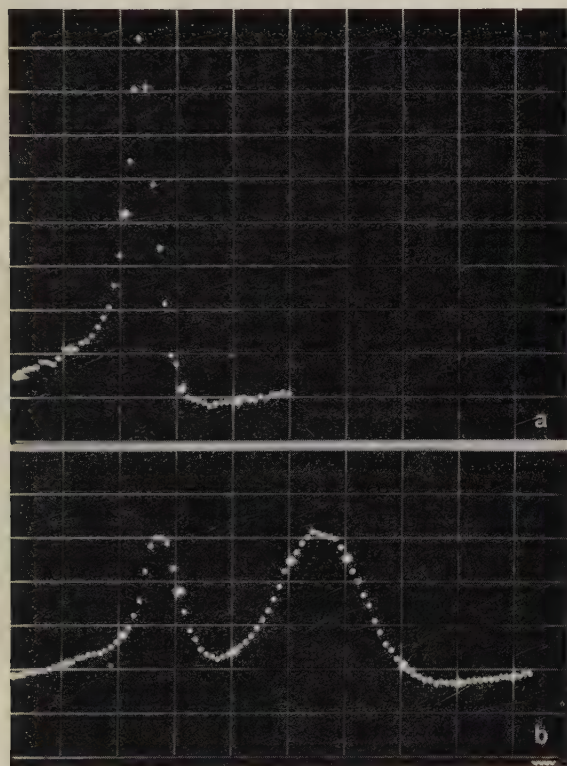


Fig. 7. Typical concentration profile measurement using the 629 keV resonance of $^{18}\text{O}(p,\alpha)^{15}\text{N}$. a) Thin target excitation curve; b) yield curve for an ^{18}O - ^{16}O - ^{18}O Ta_2O_5 "sandwich" target. 390 eV/channel, 5×10^3 counts/division.

Fig. 7 shows a typical case encountered when using ^{18}O tracing to study oxygen transport during anodic oxidation of tantalum. Fig. 7a shows a detailed excitation curve of the reaction $^{18}\text{O}(p,\alpha)^{15}\text{N}$ in the vicinity of the 629 keV resonance, at $\theta = 150^\circ$ (see fig. 1b), obtained with a 70 Å thick Ta_2O_5 film enriched to 80% ^{18}O (mean beam energy loss 650 eV). The width of this resonance is, at 165° , $\Gamma = 2.5$ keV. Technical details of the method of tracing such excitation curves automatically will be given below. Fig. 7b shows the yield curve for a tantalum sample which was oxidised: up to 30 V in 80% ^{18}O enriched water, then up to 90 V in natural water, then again up to 100 V in ^{18}O enriched water. In the conditions used for anodic oxidation (5 mA/cm² constant current, interrupted when the potential V_{ox} is reached), the oxidation to a potential V_{ox} yields a film of thickness proportional to V_{ox} , at the rate 14 Å/V. The two well resolved peaks in fig. 7b show clearly that the oxidations in labelled solutions yield ^{18}O labelled films, whereas that in natural solution provides no ^{18}O , the order of the oxygen atoms being conserved. Thus the film contains (from surface towards the metal i.e. increasing bombarding energies) 140 Å ^{18}O oxide + 840 Å ^{16}O oxide + 520 Å ^{18}O oxide. Detailed analysis of similar results shows that the mixture between labelled and non labelled layers in the films extends only to some tens of Ångströms³⁰); in fig. 7b the depth resolution may be estimated to about 200 Å in Ta_2O_5 .

The use of very narrow resonances allows even better depth resolutions near the surface to be achieved; here the lower limit of the resolution is set only by the energy spread of the beam. Fig. 8 shows a typical result obtained with the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ resonance at 992 keV. The natural width of this resonance is $\Gamma = 100$ eV

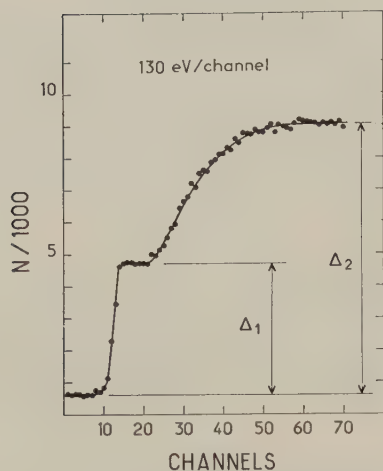


Fig. 8. Typical excitation curve of the $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ resonance near 992 keV for a 475 Å thick Al_2O_3 film on 0.8 μm aluminium.

and the beam energy spread was in this case about 250 eV. The target is a 0.8 μm thick evaporated aluminium layer on tantalum backing, which was anodically oxidised in natural water to $V_{\text{ox}} = 40$ V at a constant current of 10 mA/cm²; the oxide film is 475 Å thick, if the composition is Al_2O_3 . The γ-rays were detected with a 3" × 3" NaI(Tl) scintillator at 10 cm, with an energy window from 1.3 to 13 MeV. The sharp rise and the good plateau show an overall energy resolution (resonance composed with beam energy spread) of about 300 eV corresponding to a depth resolution of about 60 Å in Al_2O_3 . The penetration of the beam in the bulk aluminium layer is clearly seen; the slow rise is due to energy straggling in the oxide film. It may be shown that the height Δ of the jump (as measured at the plateau) at a resonance is proportional to the inverse of the stopping power of the medium *per reacting atom*. This is why the jump is smaller in the oxide than in the metal. The ratio Δ_1/Δ_2 may be calculated from known stopping powers²⁹). For the composition Al_2O_3 one finds 0.478. From fig. 8 we get $\Delta_1/\Delta_2 = 0.485$; this proves that the stoichiometric composition of the 475 Å thick oxide is Al_2O_3 indeed and that the assumption that the film has the composition $\text{Al}(\text{OH})_3$ may be rejected. The latter hypothesis would lead to $\Delta_1/\Delta_2 = 0.275$. To sum up, the resonance method allows a precise measurement of stoichiometry on films only some hundreds of Ångström thick.

2.5. TWO-DIMENSIONAL ANALYSIS OF PROFILES

In the preceding section we dealt with relatively thin targets and all the emitted particles were detected. Thus the energy spectrum of the α-particles corresponding to

fig. 7b was a slightly broadened peak. On the other hand for deep concentration profiles and for a non-isolated resonance one gets broad energy spectra as in

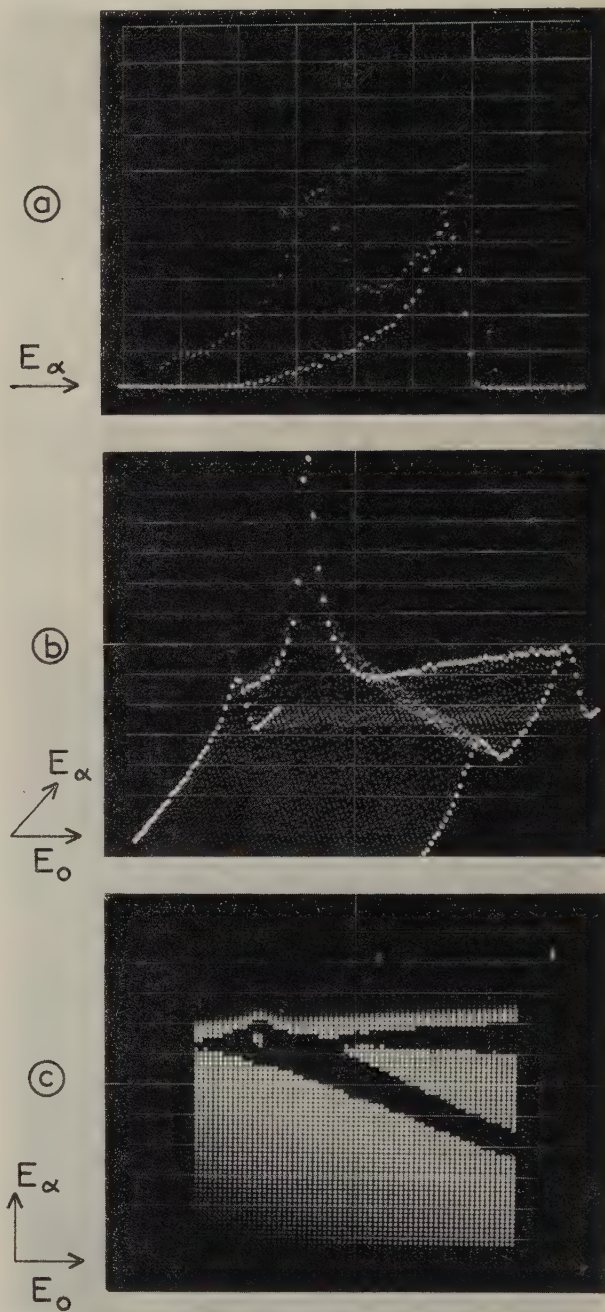


Fig. 9. Two dimensional profile analysis on ^{18}O diffused ZrO_2 target using the 629 keV resonance of $^{18}\text{O}(p,\alpha)^{15}\text{N}$. a) Energy spectra for $E_0 = 614$ keV and $E_0 = 685$ keV (double peak); b) excitation surface with 1.1 keV/channel along the E_0 axis; note the resonant shape of the cut at constant E_α ; c) horizontal cut of the surface b), emphasizing the appearance of the double peak for E_0 above the resonance.

fig. 5. The shape of these spectra depends on the bombarding energy E_0 according to eqs. (6) and (7). In particular the peak on the left in fig. 5 appears only above the resonance energy, at 629 keV for the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction. For increasing E_0 , this peak appears at decreasing α -particle energies E_α , corresponding to larger depths, at which the resonance energy is reached by the slowing down protons (see fig. 6). Fig. 9a shows two spectra obtained at 614 and 685 keV on a zirconium oxide layer. This layer was formed by thermal oxidation of zirconium in natural oxygen at 800°C for 8.6 h (11.5 μm ZrO_2), and was further heated (after cooling down) for 40 min in 95% ^{18}O enriched oxygen at 850°C (additional growth 0.4 μm). The curve at 685 keV presents two peaks, the peak at the right being much higher relative to that at the left than in fig. 5. This corresponds to a sharply decreasing diffusion profile $C(x)$, characteristic of the oxygen self-diffusion phenomenon in ZrO_2 . The curve at 614 keV, below the resonance, presents of course only one peak.

The precise analysis of the change of the shapes of the α -energy spectra (like those in figs. 5 and 9a), when E_0 passes a resonance of the cross section, allows one to combine the methods of sections 2.3 and 2.4 and yields maximum information on $C(x)$. This is achieved by using a two-dimensional memory, the spectra corresponding to various energies E_0 being stored sequentially. The automatic energy scanning system described below allows this operation to be carried out easily. Fig. 9b shows the resulting surface around the 629 keV resonance, with cuts parallel to the E_α axis (the spectra shown in fig. 9a), and to the E_0 axis (at constant E_α). The last curve is in fact the excitation function of the higher energy α -particles; its small width, about 5 keV, shows that $C(x)$ is sharply peaked near the sample surface. Fig. 9c is a horizontal cut through the "excitation surface". It shows clearly how the second peak at the left in the α -energy spectra appears above the resonance energy and how its position is shifted towards lower energies E_α with increasing E_0 . A detailed analysis of the surface of fig. 9b gives information on $C(x)$ both at small and at larger depths, simultaneously.

2.6. ELASTIC SCATTERING

The principles described above may be applied to elastic scattering of charged particles. ^4He or ^{12}C beams are generally used for such work. The analysis of the spectra allows to measure the stoichiometry of films some thousand Ångström thick in a way analogous to that of fig. 8³¹). Concentration profiles may also be

measured in this way as illustrated in refs. 26 and 32. Considering the extensive use of elastic scattering in the study of channeling phenomena in recent years we shall not illustrate here this method in more detail.

2.7. REFERENCE STANDARDS

The construction of reliable reference standards is one of the fundamental problems of nuclear microanalysis. For oxygen, both ^{16}O and ^{18}O , anodic oxidation of tantalum provides an easy way to obtain thin films of high uniformity and of well-known composition^{2,11,33}). Nitrogen standards may be obtained by reactive sputtering of tantalum¹⁴), whereas LiF and CaF_2 targets are used for lithium and fluorine²⁸). A detailed discussion of this problem is beyond the scope of this paper.

3. Experimental

3.1. THE BEAM HANDLING SYSTEM

The accelerator is a conventional, horizontal AN 2000 2 MeV Van de Graaff generator with an extra-long tank. The ion source may be switched to four different gas bottles. Two electrostatic beam steerers allow the correct centering of the beam on a slit assembly located at 135 cm from the tank base, both in the horizontal and vertical directions. The beam passes then through a Model 1050 2 inch Varian double quadrupole lens. A circular pole switching and analysing magnet (Varian Model 1036, 9.5 inch field radius, 15 kG at 155 A, mass energy product $ME/Z^2 = 35$ at 45°) allows a correct focusing of the beam in any exit direction, with the quadrupole system located in front of the magnet. 6 exit pipes symmetrically located with respect to the accelerator axis are available at angles 45°, 31°49' and 18°22'. The first two angles are in the ratio $\sqrt{2}$, the second and third in the ratio $\sqrt{3}$. This allows simultaneous extraction of two beams with ions of different mass or charge state, a convenient possibility, in particular when handling very small currents: one beam may be used for the experiment, the other for energy stabilization. The field in the magnet is measured with a Varian FR-40 Hall effect gaussmeter; this allows a very quick setting of the field and is preferred to a magnetic resonance set up.

Energy stabilization is by a Varian Model 9024 slit feedback system with a capacitive pick-off fast feedback loop. The ultimate energy stability may be limited by the mechanical vibrations of the high voltage terminal and for new facilities two symmetrically located capacitive pick-off plates should be foreseen, to compensate for this effect. The specially designed slits are carefully shielded to avoid pick-up, and are not

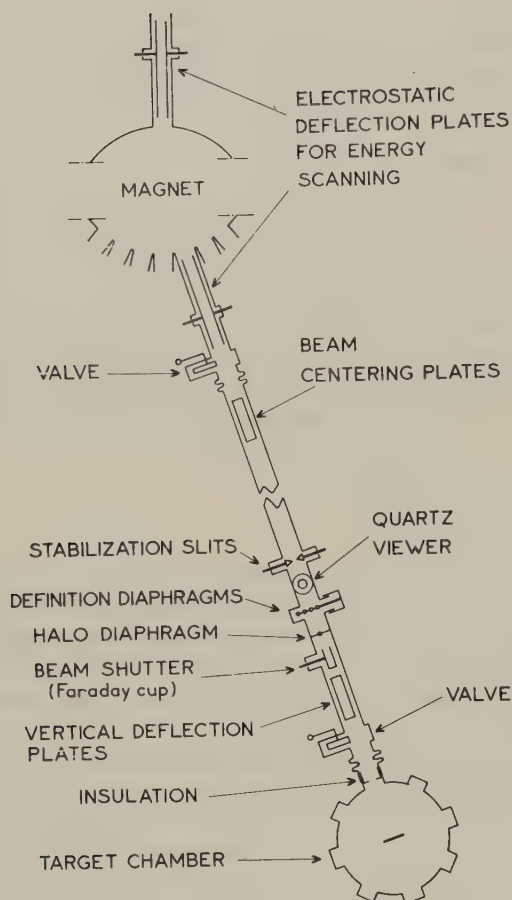


Fig. 10. Typical lay-out of a beam pipe.

water-cooled to eliminate leakage effects. High frequency sparking of the corona points is prevented by injecting in the conventional $\text{N}_2\text{-CO}_2$ mixture (proportion 4 to 1) 2% of SF_6 gas; this is an essential condition for small energy spread. With a good belt and with optimal settings the best energy resolution with this set up achieved until now was 150 eV fwhm at 18° deflection angle and with a $1\ \mu\text{A}$ current; this was measured directly with the $^{27}\text{Al}(\text{p},\gamma)^{28}\text{Si}$ resonance at 992 keV, with a target similar to that of fig. 8. Usually the resolution is around 200 eV.

Fig. 10 shows a typical beam handling system at the exit of the magnet. The beam centering plates allow centering of the beam in the vertical direction when necessary. The halo diaphragm stops particles which were scattered by the edge of the definition diaphragm as well as secondary electrons emitted by the latter. The beam shutter automatically stops the beam for sensitive targets when the measurement is over, while still providing a good indication of the current. The

vertical deflection plates allow automatic position scanning of the target (see below). They are 130 mm long, 30 mm wide, with 11 mm spacing. This gives, typically (for a distance from the center of the plates to the target of 50 cm), a 1 mm spot displacement for 250 V applied potential for a 730 keV proton beam. Fig. 11 shows a close view of the beam extensions near the scattering chambers, illustrating fig. 10. The beam currents used in the various experiments range from some nanoamperes (for elastic scattering) to $1\ \mu\text{A}$. The usual definition diaphragm is of 1 mm diameter; 0.5 and 1.5 mm diaphragms are used in some experiments.

The automatic energy scanning is by two pairs of electrostatic plates located at the input and the output of the magnet. The system is digitally controlled by a stepping motor which acts on a digitalized high voltage supply. The theory of this energy scanning system and full details of construction and use will be published in the near future³⁴.

3.2. PARTICLE DETECTION TECHNIQUES

Silicon surface barrier detectors, with coaxial mount from Ortec, of surface area ranging from 0.25 to $3\ \text{cm}^2$ are used. The detection angle is 150° for high sensitivity measurements. This allows a $3\ \text{cm}^2$ detector to be placed at about 5 cm from the target. When precise energy spectra are to be registered the detection angle is 165° and the distance about 10 cm: this minimises the energy spread due to the kinematics and to longer paths through the absorber of particles which are not perpendicular to the detector surface. A nylon diaphragm precisely delimits the regions of the detector which are fully sensitive. Care should be taken to *avoid channeling* effects when examining single crystals; in this case either the angular position of the target or that of the detector should be modified, if necessary.

The absorbers used to stop the elastically scattered beam particles are made with mylar foils of convenient thickness. They are stretched on independent frames which may be interchanged according to the requirements of the experiments. To estimate the thickness of mylar required to stop particles of a given energy an approximate relation is used according to which $1\ \mu\text{m}$ of mylar is equivalent to 1.32 mm of air. The range-energy relations for the latter are well known³⁵). Typical mylar thicknesses may be found in table 2. For concentration profile measurements the transmission characteristics of the absorber should be directly determined, if high precision is required. The relation $E_2 = f(E_1)$, where E_1 is the particle energy before and E_2 after the mylar, is measured by an ab-

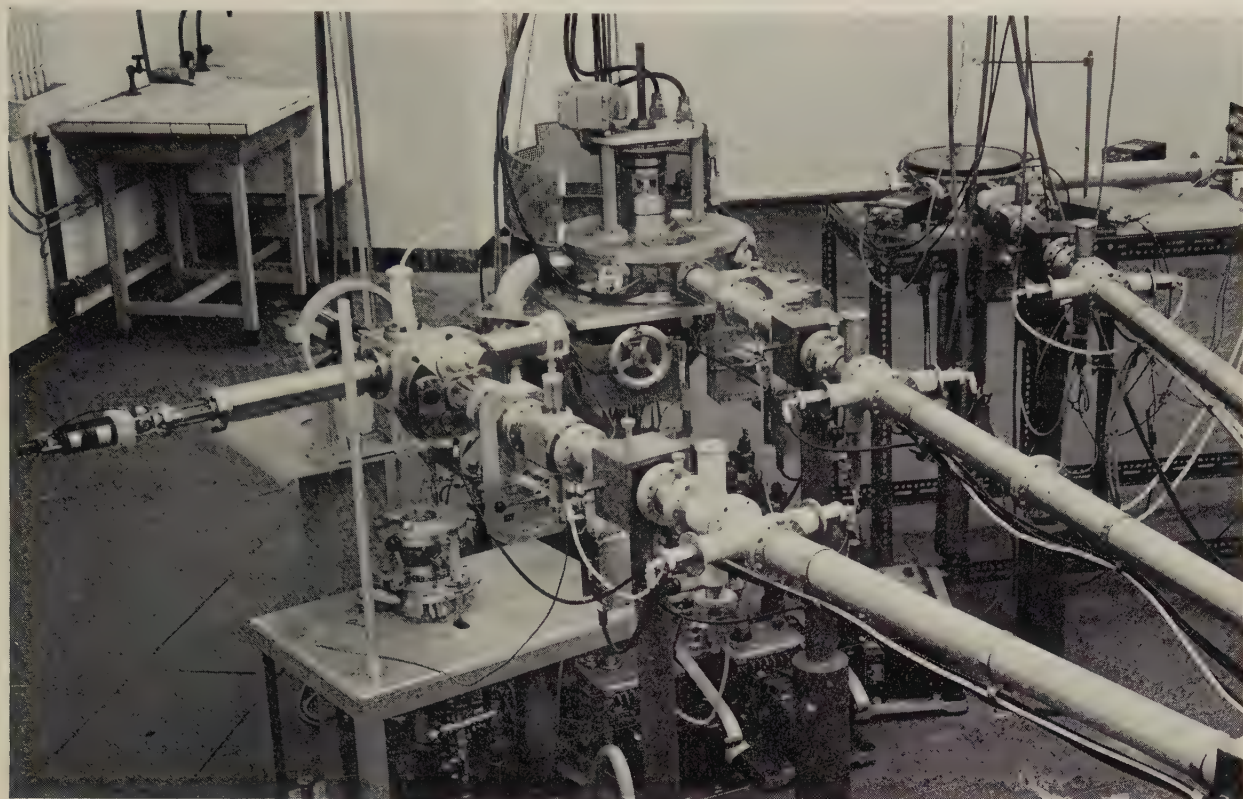


Fig. 11. A view of the beam handling systems and of the scattering chambers.

solute calibration of the energy scale at the detector output. This is achieved by detecting particles elastically scattered from a thin gold layer on aluminium backing, the mylar being removed, and the beam current being very small. The side of the mylar foils facing the target is slightly aluminised (commercially available), and the frame is electrically connected to the scattering chamber (see below).

The thickness of the sensitive zone of the detector should be adjusted to the energy and nature of the particles to be detected. It often happens that high energy proton peaks mix up with the α -particle peaks to be observed. In this case a thin enough sensitive zone should be used, so that the high energy protons lose only a small part of their energy in this zone³⁶. Fig. 12 illustrates this effect for the deuteron induced reactions on ^{14}N , in conditions identical to those of fig. 3. In fig. 12a the high energy proton group ($E_{p_0} = 8.5$ MeV) leads to a peak just below the α_1 peak, for a 300 μm thick sensitive zone (detector resistivity 4700 Ω cm, surface 3 cm^2 , bias 75 V). In fig. 12b the same peak is below the $p_1 + p_2$ doublet peak, for a sensitive zone of 230 μm (bias 40 V); the α_1 group is now completely isolated (fig. 12b is a detail of fig. 3). It may be

seen that the peaks corresponding to particles stopped in the barrier practically did not shift (with a charge sensitive amplifier), and that the p_0 peak is much broadened owing to energy straggling effects, a small part of the energy of p_0 being only lost in the barrier.

Another situation where thin sensitive zones should be used is when low energy particles are detected in presence of intense β -ray radioactivity induced in the target. Fig. 13 shows such a situation, when detecting protons from the $^{16}\text{O}(\text{d},\text{p})^{17}\text{O}$ reaction emitted from a 900 $\text{\AA}$ thick Ta_2O_5 target enriched to 90% ^{18}O . A 19 μm thick mylar absorber must be used to stop α -particles from the $^{18}\text{O}(\text{d},\alpha)^{16}\text{N}$ reaction. Curve 2, registered with a 230 μm thick sensitive zone (same detector as in fig. 12), is strongly perturbed by an exponential like β -ray background spectrum from the decay of ^{16}N [from $^{18}\text{O}(\text{d},\alpha)^{16}\text{N}$] and ^{19}O [from $^{18}\text{O}(\text{d},\text{p})^{19}\text{O}$]. In curve 1 this effect is much reduced with a 60 μm thick depletion zone (bias 3 V). The proton peak is somewhat shifted and broadened owing to the large capacitance of the 3 cm^2 detector at such a low bias.

Detector signal handling is usually conventional; the detectors are connected to a 109 A Ortec charge

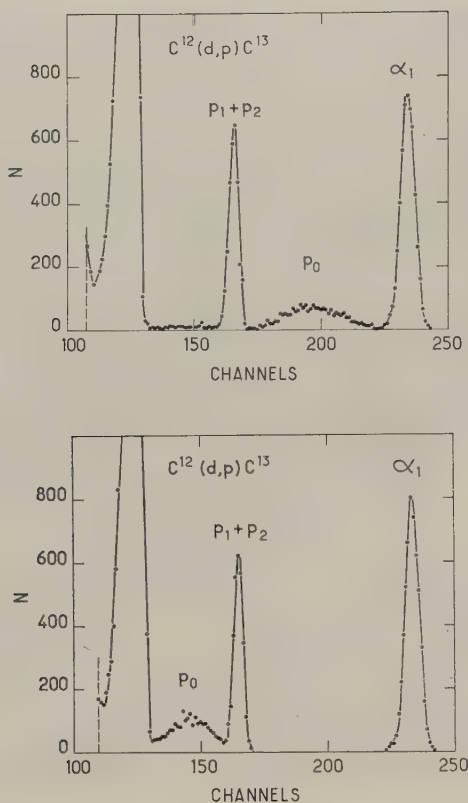


Fig. 12. Influence of the detector barrier thickness on the position of a peak from a high energy proton ($^{14}\text{N} + \text{d}$ reactions, see fig. 3). a) $300\ \mu\text{m}$ barrier; b) $230\ \mu\text{m}$ barrier; the α_1 peak is here completely isolated. $16.5\ \text{keV/channel}$.

sensitive preamplifier through an, as short as possible, $100\ \Omega$ characteristic impedance (to reduce cable capacitance), coaxial cable. Pile up effects should be carefully avoided when the shape of the spectra must be faithfully registered. With modern equipment, electronic noise presents generally no problem for heavy charged particle detection.

Sophisticated electronic equipment should be used in some special cases. Thus when using the $1165\ \text{keV}$ narrow resonance of the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction¹⁵, for high resolution depth measurements of ^{18}O , the range of the protons is larger than that of the α -particles. The latter must be detected at 165° as the resonance cross section is strongly backward peaked. A high speed amplifier with a 10 to 20 nsec clipping time, specially designed for this purpose, is then used; it allows one to handle up to several 10^7 proton background counts per second and yet to isolate the α -particle peak. All the details of this set-up and of its use in such experiments are described in ref. 37.

3.3. ELECTRONIC SET-UP

Most of the operations for nuclear microanalysis are carried out automatically. For this purpose all the mechanical movements in the scattering chambers (see below) are digitally controlled through stepping motors. The potentials applied to the electrostatic plates for vertical beam scanning, or for energy scanning, are also controlled by a stepping motor, as mentioned above. A simplified block diagram of the electronic set-up is shown in fig. 14. The Model 1000 Brookhaven Instruments digitizing current integrator acts as the central clock which controls all the operations so as to ensure that each counting corresponds to the same beam charge. Once the preset charge is reached, the counting system is inhibited, the contents of the scalers are read out, and the preset pulse train generator acts on the stepping motor to set it in its next position. The cycle begins again once both the read out and the pulse train are over. Simultaneously, in the case when the spectrum is also registered at each position, the address register of the two dimensional memory (a BM 96 Intertechnique unit) is incremented. In other cases all the information is stored in the memory block and the scalers are not read out; this may reduce the time intervals between measurements. Dead time losses of the ADC are corrected for by operating it in coincidence with a fast single channel analyzer. N_0/N_s yields the correction factor.

A specially designed digital single channel analyzer is directly connected to the digital output of the ADC. It allows integration, on line, of the content of the

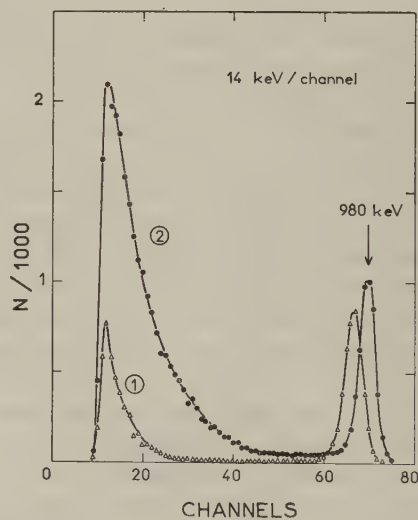


Fig. 13. Influence of the detector barrier thickness on the β -ray background. Protons from $^{16}\text{O}(d,p)^{17}\text{O}$ reaction, $19\ \mu\text{m}$ mylar. 1) $60\ \mu\text{m}$ barrier, 2) $230\ \mu\text{m}$ barrier.

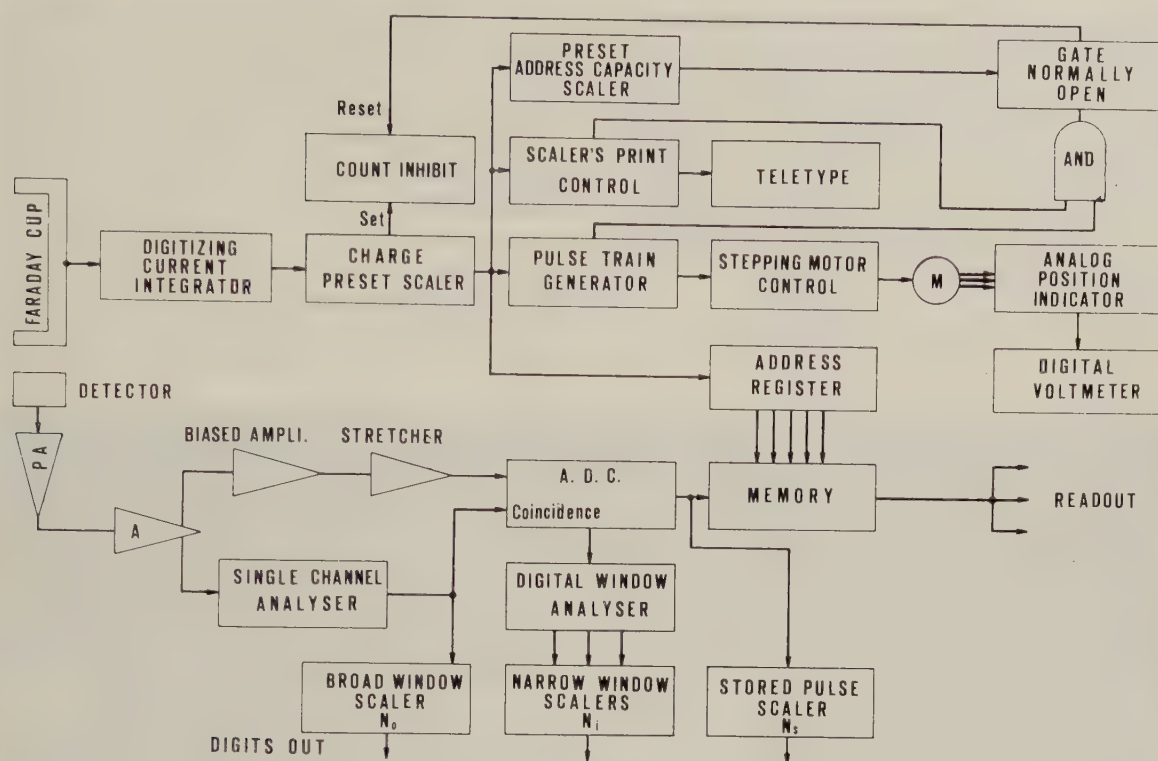


Fig. 14. Simplified block diagram of the electronic set-up.

channels between any pair of preset addresses. This device is most practical for nuclear microanalysis as it avoids the tedious operations required to set analog windows on the peaks of interest. It has a capacity of four independent windows and allows the on-line treatment of complex spectra without the use of a computer.

The complete system allows the simultaneous control of several stepping motors, and permits bidirectional movements and backlash compensation. The set-up is routinely used for automatic microanalysis of up to 80 samples, topographic exploration (see below), automatic energy scanning, the digitized control of a goniometer for channeling experiments, etc.

3.4. SCATTERING CHAMBERS

We shall describe briefly the general principles which were followed when constructing the various scattering chambers used for nuclear microanalysis. The target holders contain as many samples as possible. Large windows allow easy observation of the interior. Various absorbers, positioned from outside, may be inserted in front of the detectors. Several detectors are installed simultaneously in each chamber. The samples are easy to translate and if necessary to tilt. Usually the samples are perpendicular to the beam ($\phi = 0$).

A basic problem is beam current integration. Owing to the mechanical complexity of these chambers the targets are electrically connected to them (insulating targets should be slightly coated with a conductor film, to avoid breakdown). There is no secondary electron suppressor in the chambers. The following precautions are taken against secondary electrons and leakages:

- The chamber is completely insulated: the detectors are supported by specially designed vacuum tight nylon holders; the stepping motors are connected and supported by nylon axes; for the precise measurement of small currents a glass tube separates the chambers from the accelerator and from the pumps.

– A good vacuum is maintained (some 10^{-6} mm Hg) by oil diffusion pumps, with a zeolite trap on the primary pump: this minimizes carbon deposition on the targets and avoids, as compared to mercury pumps, the danger of mercury vapors for the gold covered detectors. Additional cold traps inside the chamber are used in some cases.

– A 1 cm diameter diaphragm at the entrance of the chamber stops secondary electrons but still allows vertical beam scanning. The metallised mylar absorbers connected to the chamber prevent electron

escape to the detectors. When no absorber is used the whole detector assembly may be connected to the chamber; the preamplifier is then powered from a battery and the signals are transmitted through an insulating pulse transformer. A wide mesh metallic grid prevents electron escape towards the pumps.

The chambers are thus good Faraday cups. Pick-up effects on the current integration are not observed owing to the very low input impedance of the integrator used.

Fig. 11 shows three such chambers each of them designed for special tasks. The closest chamber is highly

insulated with glass tube supports; it is designed for high precision registration of spectra. It may contain up to 18 samples 15 mm long, which may be tilted for depth magnification. An NaI(Tl) γ -ray detector may be placed very close to the target. Thin self-supporting targets may be introduced in this chamber.

Fig. 15 shows a close view of the chamber used for automatic routine microanalysis (at the right on fig. 11). It may contain up to 80, 15 mm long samples, fixed on interchangeable holders. The chamber may be loaded within some minutes. Three 3 cm² detectors at 50 mm and at 150° yield a total solid angle of about

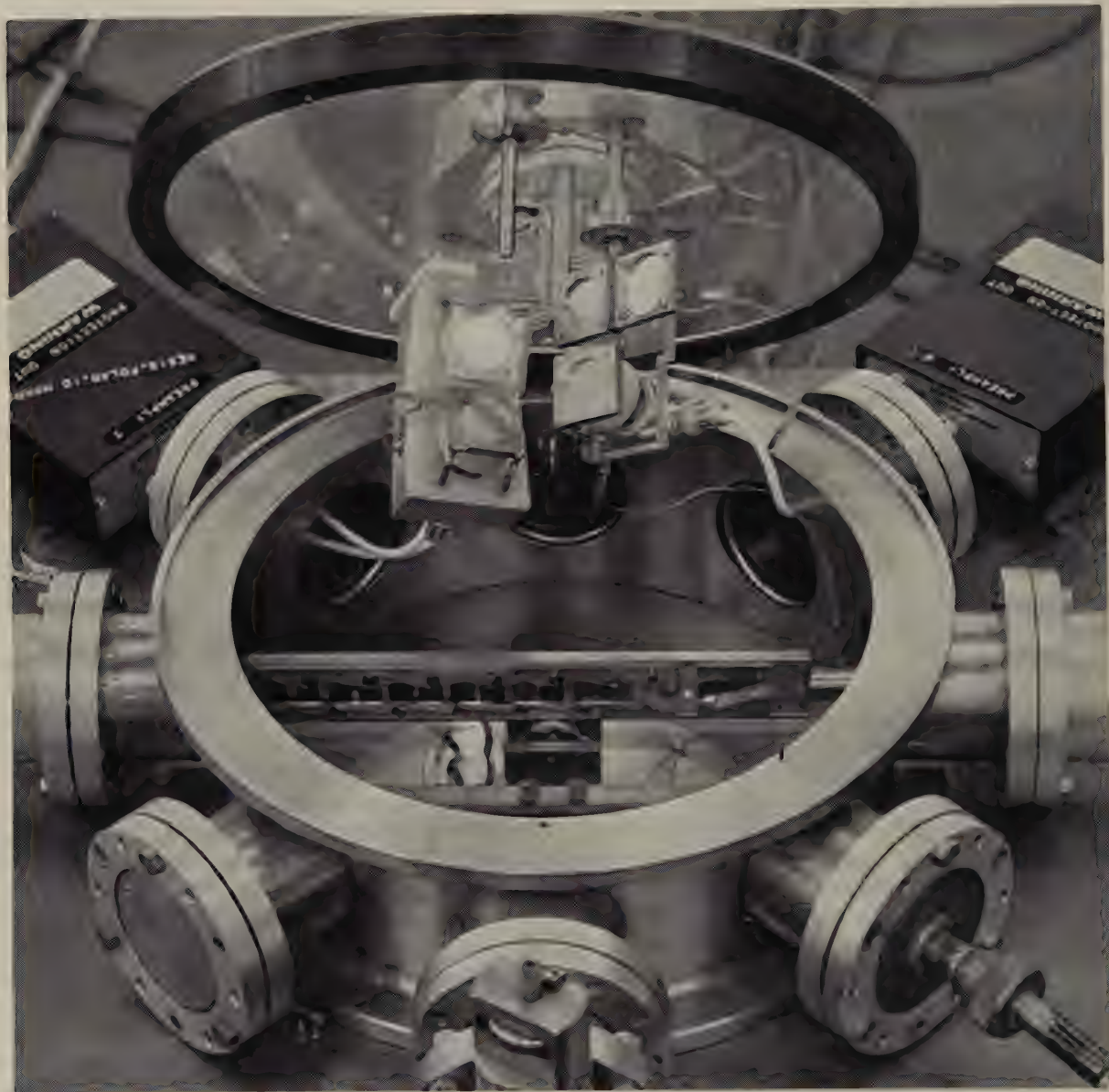


Fig. 15. A close view of the 80 samples capacity scattering chamber used for routine microanalysis.

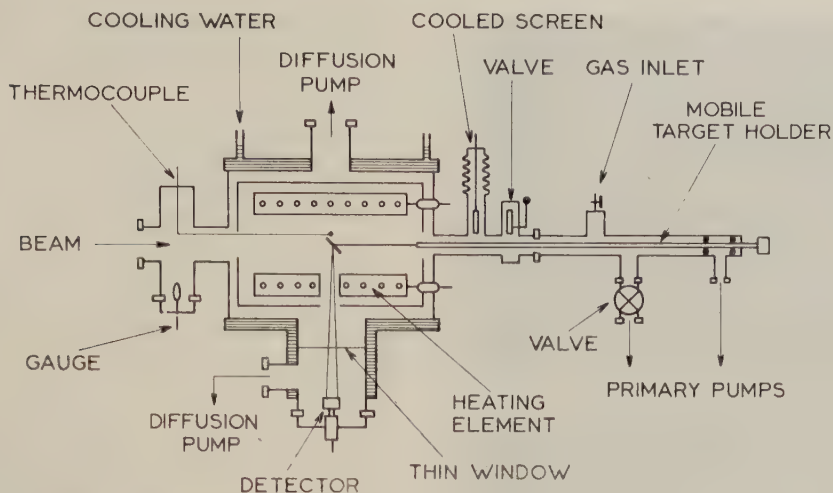


Fig. 16. Schematic diagram of the furnace directly coupled to the accelerator.

0.3 sterad, insuring high sensitivity. The absorbers may be changed from outside for one of these detectors. The top is made with transparent perspex; it should be obscured when the detectors are operating, to avoid light induced reverse currents.

In the second chamber, in fig. 11, 10 samples may be introduced without breaking the vacuum. The samples first pass through a fore-vacuum chamber, and are introduced after one minute into the high vacuum by a pneumatically operated system. This chamber allows a quick recycling of samples which undergo chemical or electrochemical treatment: after each treatment the sample may be analysed within some minutes.

Fig. 16 shows schematically a furnace directly connected to the accelerator, which allows diffusion phenomena to be followed as they proceed. A differential pump allows one to introduce gases up to pressures of the order of a tenth of a $\mu\text{m Hg}$. Maximum temperature is 900°C ; 10^{-5} mm Hg vacuum may then be reached. The thin window is made of aluminium or metallized capton foils, which allow one to extract the particles from reactions on ^{16}O or ^{18}O , while reflecting heat and light. A 1 kW insulated alternator provides a floating power source, which allows current integration.

A fully automatized 3 axis goniometer for channeling studies, constructed following the same principles, completes the facility. It will not be described here.

4. Applications

Several applications were shown above to illustrate the principles of the method. We present here some more results and a short list of other possible applications.

Fig. 17a shows a topographic scanning of the ^{16}O

content of a tantalum sample anodically oxidised by steps of 20 V from 0 to 100 V. The stepping motor was used to translate the sample. The lateral concentration profile appears with precision; the spot diameter was 1 mm. Fig. 17b shows a method of measuring beam spot diameter and position. The target holder of the chamber of fig. 15 supports a trapezoidally shaped ^{18}O enriched oxide target (which may be seen on fig. 15, at the right). The geometry is shown in fig. 17c. When the target is translated, the rise of the ^{18}O or ^{16}O yield (measured with a proton or deuteron beam) near the vertical side of the target corresponds to the beam spot diameter directly, whereas the oblique side leads to a magnification by a factor of $1/\sin \alpha \approx 3.5$. This effect is striking on fig. 17b; the sharp rise indicates a beam spot diameter of about 1 mm; the slower rise gives the more precise figure of 1.3 mm containing 90% of the beam. As the definition diaphragm was at 86 cm and of 1 mm diameter, this gives a measure of the beam divergence, of the order of 0.3 mrad. The distance between the rise and fall of the curve in fig. 17b (fwhm) is proportional to the beam height, as seen in fig. 17c. This allows an easy centering of the beam. This is of great help for precise topographic measurements (or for small samples), when dangerous radiations preclude the use by the experimenter of a quartz viewer (deuteron beams). The beam position and size information is in any case much more precise.

Fig. 18 shows a typical result obtained with the furnace of fig. 16. A Van Arkel type zirconium sample containing 60 ppm of oxygen was heated in 10^{-5} mm Hg vacuum at 700°C . The sample was previously polished in a mixture of fluorhydric and nitric acid. The $^{16}\text{O}(\text{d,p})^{17}\text{O}$ reaction was observed at 90° and

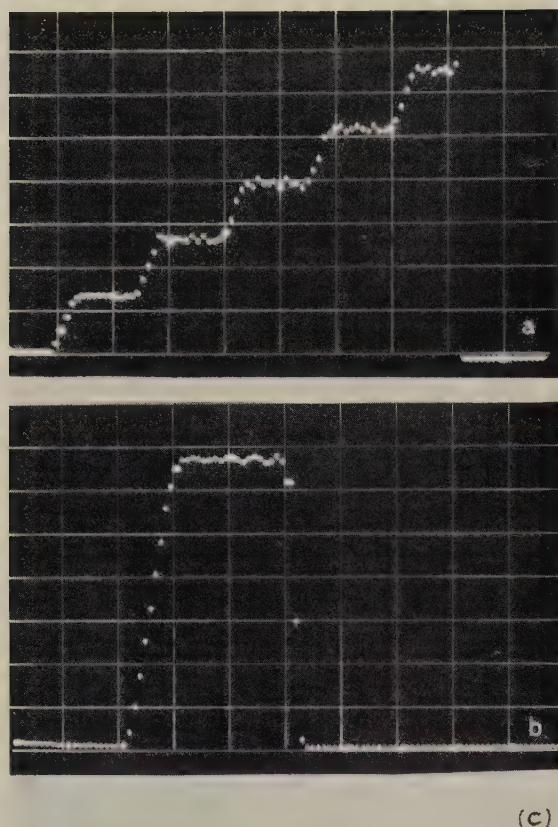


Fig. 17. Lateral topographic scanning. a) Non-uniform tantalum oxide, 0.25 mm/channel; b) beam size and position measurement with a target of shape shown in c): $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reaction, 0.5 mm/channel.

at 1.2 MeV bombarding energy. The curves of fig. 18 correspond to the same charge. The peak in the curve 1, recorded at room temperature, is characteristic of a very thin oxide layer on the surface; the small tail corresponds to the 60 ppm oxygen in the metal. Curve 2, recorded after about 3 min at 700°C , shows a strong increase of the oxygen on the surface and a marked diffusion inside the metal. Curve 3, recorded after 105 min treatment indicates a very deep diffusion in the metal, whereas the oxygen content near the surface markedly decreased, well below the content of the natural oxide layer on zirconium at room temperature.

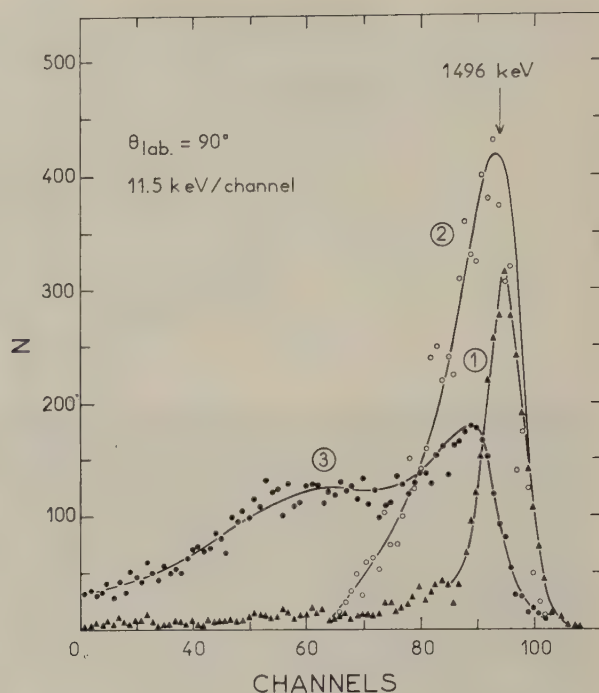


Fig. 18. A typical application of the furnace of fig. 16: oxygen diffusion in zirconium at 10^{-5} mm Hg vacuum. 1) Spectrum before heating; 2) after 3 min at 700°C ; 3) after 105 min diffusion, exhibiting deep oxygen penetration.

A systematic study of the oxidation of zirconium at very low pressures is in course along these lines.

Fig. 19 shows an excitation curve of the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ reaction near the very narrow resonance ($\Gamma < 100 \text{ eV}$) at 1165 keV, recorded with the method mentioned above. The target is an aluminium sample anodically oxidized in a way similar to the sample of fig. 7: up to 20 V in an 80% ^{18}O enriched solution, then up to 55

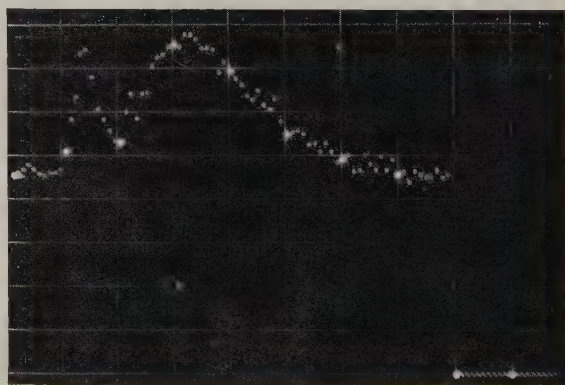


Fig. 19. High resolution excitation curve of the $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ narrow resonance at 1165 keV on an ^{18}O - ^{16}O - ^{18}O Al_2O_3 "sandwich" target. 130 eV/channel, 300 counts/div.

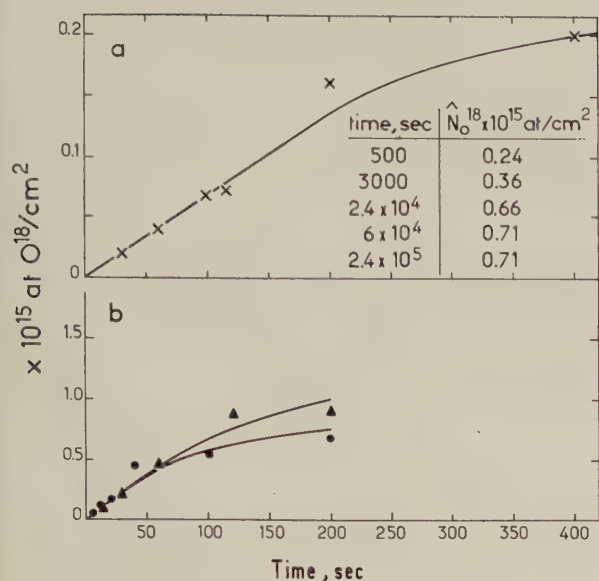


Fig. 20. A typical application to the determination of submonolayer ^{18}O oxide quantities: kinetics of isotopic exchange with an ^{18}O labelled solution: a) of tantalum anodic oxide; b) of aluminium anodic oxide (● polished and ▲ unpolished aluminium).

V in a natural solution and up to 60 V in an ^{18}O enriched solution again (Al_2O_3 film thickness 12 Å/V in these conditions). The very sharp peak at the left (650 eV fwhm) indicates that the last oxidation merely added an ^{18}O labelled oxide layer to an intermediate non-labelled layer. As an indication, the mean energy loss in a 5 V (60 Å) thick film is 350 eV and the beam energy spread was about 250 eV. Fig. 19 qualitatively shows that, as for tantalum in fig. 7, the order of the oxygen atoms is conserved, although the broad peak at the right may indicate some mixture. The detailed theoretical interpretation of such spectra is in progress.

Nuclear microanalysis was systematically used by our group to study anodic oxidation phenomena^{11, 15, 30, 33, 38, 39}). As an illustration of the sensitivity of the method, we show in fig. 20 the kinetics of the isotopic exchange between anodic oxide films of tantalum or aluminium and an 80% ^{18}O enriched water solution. The oxides were formed in ^{18}O depleted water (0.007% ^{18}O) to minimize their ^{18}O content. The limiting value of the ^{18}O uptake for Ta_2O_5 is $0.7 \times 10^{15} \text{ at/cm}^2$, i.e. one monolayer. Thus detailed kinetic studies of submonolayer quantities may be easily performed.

Other applications are currently in electrochemistry⁴⁰), metallurgy^{3, 13, 41}), surface treatment studies⁴¹), and mineralogy⁴²).

The authors wish to thank M. Vidal and B. Lavernhe for their assistance in the installation and operation of the accelerator. The efficient cooperation with H. Gladieux, J. Parizel and C. Tourneville for the construction of the scattering chambers was highly appreciated. They are grateful to J. P. Enard for his help in problems related to mechanics and vacuum. Collaboration with the physicists using this method: C. Cherki, M. Croset, D. Dieumegard, B. Maurel, C. Ortega, S. Rigo, J. Siejka was most helpful. The contribution to the experiments on zirconium of G. Béranger and P. Boisot is gratefully acknowledged.

References

- 1) G. Slodzian, *Rev. Phys. Appl.* **3** (1968) 360.
- 2) G. Amsel and D. Samuel, *Anal. Chem.* **39** (1967) 1689.
- 3) G. Amsel, D. David, G. Béranger and P. Boisot, *Rev. Phys. Appl.* **3** (1968) 373.
- 4) G. Cabane and C. Engelman, *Rev. Phys. Appl.* **3** (1968) 365.
- 5) P. Albert, C. Engelman, S. May and J. Petit, *C.R. Acad. Sci.* **254** (1962) 119.
- 6) S. S. Markowitz and J. D. Mahony, *Anal. Chem.* **34** (1962) 329.
- 7) J. B. Holt and R. H. Condit, *J. Electrochem. Soc.* **111** (1964) 1132.
- 8) J. B. Holt and L. Himmel, *J. Electrochem. Soc.* **116** (1969) 1569.
- 9) J. F. Lamb, D. M. Lee and S. S. Markowitz, *Anal. Chem.* **42** (1970) 212.
- 10) G. Amsel, LAL Report 1053 (Orsay, May 1963).
- 11) J. P. Nadai, Thesis (Orsay, 1967).
- 12) D. W. Palmer, *Nucl. Instr. and Meth.* **38** (1965) 187.
- 13) G. Amsel, G. Béranger, B. de Gelas and P. Lacombe, *J. Appl. Phys.* **39** (1968) 2246.
- 14) G. Amsel and D. David, *Rev. Phys. Appl.* **4** (1969) 383; *Internat. Conf. MIS structures* (Grenoble, June 1969) p. 243.
- 15) G. Amsel and D. Samuel, *J. Phys. Chem. Solids* **23** (1962) 1707.
- 16) R. W. Ollerhead, E. Almquist and J. A. Kneher, *J. Appl. Phys.* **37** (1966) 2440.
- 17) E. Möller and N. Starfelt, *Nucl. Instr. and Meth.* **50** (1967) 225.
- 18) T. M. Sabine, J. R. Bird and B. K. Mak, *Proc. Intern. Conf. Solid state phys. with accel.* (Sept. 1967) BNL Report no. 50083 (C-52), p. 192.
- 19) L. Quaglia, R. Robaye, M. Cuypers and J. Barrandon, *Nucl. Instr. and Meth.* **68** (1969) 315.
- 20) E. Ligeon, A. Bontemps, J. Fontenille and G. Guernet, *Microelectronics Conf.* (Paris, April 1970) p. 50.
- 21) E. Möller, L. Nilsson and N. Starfelt, *Nucl. Instr. and Meth.* **50** (1967) 270.
- 22) W. J. Naude, M. Peisach, R. Pretorius and P. J. Strebel, *J. Radioanal. Chem.* **1** (1968) 231.
- 23) S. Rubin, *Nucl. Instr. and Meth.* **5** (1959) 177.
- 24) R. D. Edge and W. F. Lankford, *Proc. Internat. Conf. Solid state phys. with accel.* (Sept. 1967) BNL Report no. 50083 (C-52), p. 167.
- 25) T. B. Pierce, P. F. Peck and D. R. A. Cuff, *Nucl. Instr. and Meth.* **67** (1969) 1.
- 26) A. Turos and Z. Wilhelmi, *Nukleonika* **13** (1968) 975; *Nukleonika* **14** (1969) 319.

- ²⁷⁾ R. R. Hart, N. T. Olson, H. P. Smith and J. M. Kahn, *J. Appl. Phys.* **39** (1968) 5538.
- ²⁸⁾ G. Amsel, D. Dieumegard and B. Maurel, to be published.
- ²⁹⁾ C. F. Williamson, J. P. Boujot and J. Picard, Tables of range and stopping power of chemical elements for charged particles, CEA Report R 3042 (1966).
- ³⁰⁾ C. Cherki, Thesis (Paris, 1969).
- ³¹⁾ M. Croset, S. Rigo and G. Amsel, to be published.
- ³²⁾ F. Abel, G. Amsel, E. d'Artemare and M. Bruneaux, *J. Phys. Chem. Sol.* **30** (1969) 687.
- ³³⁾ G. Amsel, C. Cherki, G. Feuillade and J. P. Nadai, *J. Phys. Chem. Sol.* **30** (1969) 2117.
- ³⁴⁾ G. Amsel, E. d'Artemare and E. Girard, to be published.
- ³⁵⁾ W. Wahling, *Handbuch der Physik*, vol. 33 (Springer Verlag, Berlin, 1959) p. 202.
- ³⁶⁾ G. Amsel, P. Baruch and O. Smulkowski, *IRE Trans. Nucl. Sci.* **NS-8** (Jan. 1961) 21.
- ³⁷⁾ G. Amsel, R. Bosshard and C. Zajde, *IEEE Trans. Nucl. Sci.* **NS-14**, no. 1 (1967) 1.
- ³⁸⁾ G. Amsel, C. Cherki, J. P. Nadai and J. Siejka, Spring Meeting Electrochem. Soc. (New York, 1969) p. 20.
- ³⁹⁾ G. Amsel and M. Croset, same as ref. 38, p. 24.
- ⁴⁰⁾ G. Feuillade and R. Jacoud, *Electrochem. Acta* **14** (1969) 1297.
- ⁴¹⁾ G. Amsel, G. Béranger, P. Boisot, D. David, B. de Gelas and P. Lacombe, *C. R. Acad. Sci.* **267** (1968) 301; *J. Nucl. Mat.* **29** (1969) 144.
- ⁴²⁾ A. Choudhury, D. W. Palmer, G. Amsel, H. Curien and P. Baruch, *Solid State Comm.* **3** (1965) 119.



A Study of the Oxygen Growth Laws of Anodic Oxide Films on Aluminum and Tantalum Using Nuclear Microanalysis of O^{16} and O^{18}

J. Siejka, J. P. Nadai, and G. Amsel

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Tour 23-9, Quai Saint-Bernard, Paris 5ème, France

ABSTRACT

The oxygen growth laws of anodic oxide films on aluminum and tantalum were studied using the nuclear microanalysis of the O^{16} and O^{18} isotopes. The influence of current density and surface preparation on the growth laws has been demonstrated. The correlation of the results of nuclear microanalysis of O^{16} and of coulometric measurements allowed the determination of the dissolution current density during anodic oxidation of aluminum. This dissolution current was shown to be purely electrochemical. The values of the intercepts with the potential axis of the linear growth laws show that the overpotentials at the interfaces are smaller than 0.1V for current densities from some $\mu A/cm^2$ to 10 mA/cm². Measurements of isotopic exchange of oxygen using O^{18} as a tracer allowed direct estimation of the oxygen exchange current without applied field. The results show that oxygen transfer at the oxide-solution interface, enhanced by field-induced oxygen vacancies, is responsible for the growth of the anodic film.

The growth laws of anodic barrier layers on aluminum and tantalum have been carefully investigated by numerous authors (1-8) using various methods. The published results clearly indicate that the growth laws of the anodic layers are strongly dependent on the experimental conditions of sample surface preparation and of film formation, illustrating the complicated character of the mechanisms involved. It appears that the direct measurement of the oxygen content of the anodic films as a function of various parameters could contribute to the elucidation of some of the aspects of these growth mechanisms. In addition the use of tracing techniques applied to the isotopes of oxygen may yield further information, which cannot be provided directly by classical methods, on the

electrochemical processes taking place during anodic treatments.

In this work we applied the microanalysis of the isotopes of oxygen by means of nuclear reactions to a detailed study of the anodic oxidation of aluminum and tantalum in aqueous solutions. The isotope O^{16} (natural abundance 99.758%), determined by the nuclear reaction $O^{16}(d,p)O^{17*}$, was monitored to measure the oxygen content of films formed in solutions of natural isotopic composition. In the absence of long-lived radioactive isotopes of oxygen, O^{18} -enriched compounds may be used for tracing experiments, the $O^{18}(p,\alpha)N^{15}$ reaction allowing the determination of the O^{18} isotope (natural abundance 0.204%) contained in the films. Several recent publications (9-12) deal with the application of this method to anodic oxidation processes. The techniques themselves are described in detail in ref. (13-15) and will not be pre-

Key words: oxygen, aluminum, tantalum, anodic oxidation, growth rate, O^{18} tracing, nuclear microanalysis, exchange current, interface, surface treatment.

sented here. These microanalytical techniques allow the determination, with a precision of the order of 1% even for oxide films some 10 Å thick, of the number of O^{16} or O^{18} atoms/cm² they contain, with respect to an absolute oxygen standard. As an absolute oxygen standard we used here an anodic oxide film formed on tantalum in well-defined conditions, as described in ref. (9); it was shown in this reference that precise coulometric measurements allow in this case the absolute determination of the number of oxygen atoms/cm² in the standard with a precision of about 3%.

The oxygen growth laws were measured in both natural and O^{18} -labeled solutions for various sample surface preparation procedures. The results clarify the influence of the initial layer on the metal on the growth of the anodic films. Furthermore we have tried to estimate the value of the sum of the overpotentials at the metal-oxide and oxide-solution interfaces, by measuring the intercept of the oxygen growth law with the potential axis for various oxidation currents. For tantalum, Young (1) and Vermilyea (2) found very small overpotentials, which seems to imply a high ionic exchange current at the oxide-solution interface. We have therefore attempted to measure this exchange current directly by studying the isotopic exchange of O^{18} in order to correlate its value with those of the overpotentials, found by the nuclear method, for the two metals. In addition we have tried by the nuclear method to demonstrate the existence on the samples of layers of high ionic conductivity for various methods of surface preparation and, when such layers exist, to relate their presence to the changes observed in the corresponding oxygen growth laws. We have not attacked here the problem of the mechanism of ionic transport in the oxide itself. This was dealt with in ref. (10) and will be further studied, by O^{18} tracing, in a future publication.

Sample Preparation

The aluminum used was in the form of bright rolled and annealed sheets 0.6 mm thick, of purity 99.9%. Taking into consideration on the one hand that electrochemical polishing of aluminum is known to leave on the surface of the metal a thin film which may differ in its properties from anodic barrier layers (6, 16, 17), and on the other hand that unpolished samples, although free of contamination by chemicals, might present a less well-defined state of the surface, both polished and unpolished aluminum samples were systematically studied in this work. Unpolished samples were cleaned with acetone in a vapor degreasing set-up according to the classical procedure described by Holland (18). Electropolishing of the samples was carried out so as to avoid the deleterious effects on the anodic oxidation of aluminum of contamination by chlorine (17) or by chromates (6). On the other hand, as Godard reports that SO_4 anions are less "aggressive" to aluminum than chlorine (19) we used sulfuric acid as the main polishing agent. The procedure used consisted in: (a) etching in a sodium hydroxide solution (10% by weight, 10 min); (b) dipping into a solution containing 15% trisodium phosphate and 20% disodium carbonate (10 min); (c) anodic polishing in a solution containing 20% sulfuric acid (1 min, 5 mA/cm²); (d) dipping for 10 min into the above solution; and (e) rinsing in triply distilled water. This procedure is used in industry and yields a highly brilliant surface; the corresponding results on anodic oxidation showed a high degree of reproducibility.

The tantalum used, 99.95% pure, was in the form of unannealed rolled sheets 0.2 mm thick. As in ref. (9) the samples were degreased with acetone and chemically polished for 15 sec in a mixture of 5 volumes of 95% H_2SO_4 , 2 volumes of 53% HNO_3 , and 2 volumes of 45% HF. As suggested by Young (1) the samples were then dipped for 5 min in boiling tridistilled water. The assumption of Young, according to which this leaching removes fluorine traces from the surface of polished

tantalum, was recently confirmed in our laboratory using nuclear microanalysis of F^{19} (20). Although for tantalum the polishing process seems to have less influence on the subsequent anodic behavior than for aluminum, here again polished and unpolished samples were compared in some cases.

All the samples were punched into 2 cm² rectangles by a special tool (9) insuring the reproducibility of the area. The electrical contact with the samples was made by a 0.5 mm wire as described in ref. (9) or by a special tantalum clip used by Croset (21).

The unlabeled solutions were prepared with triply distilled water of resistivity 0.5×10^6 ohm-cm, and high-purity salts provided by Merck. Oxidations were carried out at $22^\circ \pm 1^\circ C$ in aqueous solutions of 5% by weight ammonium citrate of pH 6. These solutions were prepared by dissolving diammonium citrate and by adjusting the pH with ammonia. This yields a mixture of di- and triammonium citrate solution with good buffer characteristics.

In the tracer experiments water of nonnatural isotopic composition of oxygen was used¹: either enriched to 80% in O^{18} (and about 0.7% in O^{17}) or depleted 30 times in O^{18} (0.007%). The isotopic composition of hydrogen was normalized near to the natural abundance (deuterium content <0.1%). The first O^{18} -labeled anodic oxide films on aluminum were produced by Amsel and Samuel (10). They encountered difficulties in oxidizing aluminum in small volumes of O^{18} -enriched water and succeeded to do so only by a massive adjunction of ammonia, up to pH 9 (22). It was found in this work that these difficulties were due to impurities introduced in the labeled water during the enrichment procedure: careful purification allowed the anodic oxidation of aluminum to be carried out in conditions identical to the nonlabeled case. The handling of the labeled water was carried out using a vacuum line; this allows repeated loss-free transfers of the expensive enriched water, easy purification, and prevents any isotopic exchange with the constituents of the atmosphere (23). The first stage of the purification consists of eliminating dissolved gases. The sealed ampula containing a given quantity of labeled water is broken inside a cell connected to the distillation line. This cell is placed in a mixture of solid carbon dioxide and acetone; once the water has frozen, the greatest part of the dissolved gases (O_2 , CO_2 , H_2 , N_2) are removed by pumping. In the second stage, to eliminate traces of halogens, in particular, the water was distilled over sodium contained in a glass capillary (following the procedure developed by Dostrowsky (24) at the Weizmann Institute) from ambient temperature to that of melting ice. The transfer must be carried out in several stages, between which the hydrogen formed is pumped off at CO_2 -acetone temperature. The water is then distilled from the resulting sodium hydroxide solution at ambient temperature into the oxidation cell containing the necessary quantity of salt, at the temperature of melting ice.

Salts of natural isotopic composition were used both in the O^{18} -enriched and depleted solutions: preliminary experiments using ammonium citrate enriched to 70% in O^{18} showed that at least 98% of the oxygen contained in the films formed on aluminum and tantalum in our experimental conditions come from the water in the solution used (25). In addition it was shown by Samuel (26) at the Weizmann Institute that the isotopic exchange between ammonium-citrate and water is negligible at room temperature. O^{18} -labeled solutions at pH 6 were prepared in the following way. Ammonium citrate was dissolved in an ammonia solution of pH 8 in the oxidation cell. This solution was evaporated and the remaining salt dried for 6 hr in high vacuum at room temperature. The labeled water was then distilled on the salt. This procedure yields a solution of pH 6-6.5. The final adjustment of the pH,

¹ Supplied by the Weizmann Institute, Rehovot, Israël.

if necessary, may be achieved by adding a minute amount of dry citric acid.

In all the experiments with nonnatural water a special 5 cm³ cell [described in ref. (22)] was used due to the high cost of enriched or depleted water. A special sample holder was used, described in (27), with a platinum wire cathode encircling the sample. The oxidations were carried out under atmospheric pressure, the contact with the ambients being kept to a minimum. In these conditions the drop in enrichment of the 80% O¹⁸ water was negligible during the duration of the experiments.

The anode potential was measured with respect to a reference electrode using a high impedance voltmeter (Keithley 610B, 10¹⁴ ohms). To avoid contamination of the solutions by chlorine ions from a calomel reference electrode, a mercury sulfate electrode was used. To further minimize any contamination the reference electrode was separated from the solution by a double junction of sintered glass.

For electrolytes enriched in O¹⁸, reference electrodes were not used, to avoid any possibility of isotopic exchange. The anode potential was measured with respect to a platinum cathode whose current-potential characteristics had previously been measured with respect to a reference electrode.

Most of the oxidations were carried out at constant current densities, in the range of 1-10 mA/cm², using a Harrison 6209B power supply. Once the potential V_{ox} between the anode and the reference electrodes reaches a preset value, an electronic arrangement cuts the circuit. A digital current integrator (Brookhaven Instruments Corporation, Model 1000) connected to a counting scale, gives the number of coulombs consumed during the oxidation. This integrator, designed for accelerator beam current measurements, insures a precision and absolute calibration better than 10⁻³.

In order to operate at low current densities, below 10 μ A/cm², after a constant current stage (5 mA/cm²), the potential V_{ox} was maintained constant for fixed times (10 min for tantalum, 20 min and 50 min for polished and unpolished aluminum, respectively) allowing the current to decay to small final values. This procedure kept the duration of these experiments reasonably short while minimizing the perturbing effects arising at low current densities of oxidation for aluminum, which result in the formation of porous oxide or hydroxide layers as reported in ref. (4, 28, 29) (see below).

Results and Interpretation

Nuclear microanalysis gives the numbers N_{O16} or N_{O18} of oxygen atoms per square centimeter fixed on the surface of the sample; O¹⁷ will be neglected and hence the total number of oxygen atoms per square centimeter N_O is given in any oxide film by $N_O = N_{O16} + N_{O18}$. It should be noted that when results from nuclear microanalysis are compared with coulometric results obtained on the same sample, the effects of roughness cancel out, as has been pointed out in ref. (9). For a homogeneous oxide it is possible to introduce an equivalent geometric thickness L deduced from N_O , by assigning known values to the stoichiometry and the density of the chemical compound formed as well as to the roughness factor of the underlying surface. Under such assumptions we may write

$$L = \lambda N_O \quad [1]$$

where λ is a constant. This relation allows the comparison of our results on growth laws with those obtained by other authors, who measured the thickness of the films formed by various methods such as capacitance, optical, gravimetric, etc., measurements. Let us remark that the determination of the intercepts of the growth laws with the potential axis does not depend on a given normalization of the thickness, and hence neither on the roughness factor nor on the absolute oxygen standard.

Oxygen growth laws.—General characteristics.—Figures 1, 2, and 3 show the curves $N_O = f(V_{ox})$ obtained at various final current densities between some μ A and 10 mA/cm², on polished tantalum and unpolished and polished aluminum, respectively. The values of the potentials are expressed in the hydrogen scale, in volts. The oxidations were carried out in unlabeled solutions; N_O is therefore given by N_{O16} . It should be noted that the quantities of oxygen in the initial layer

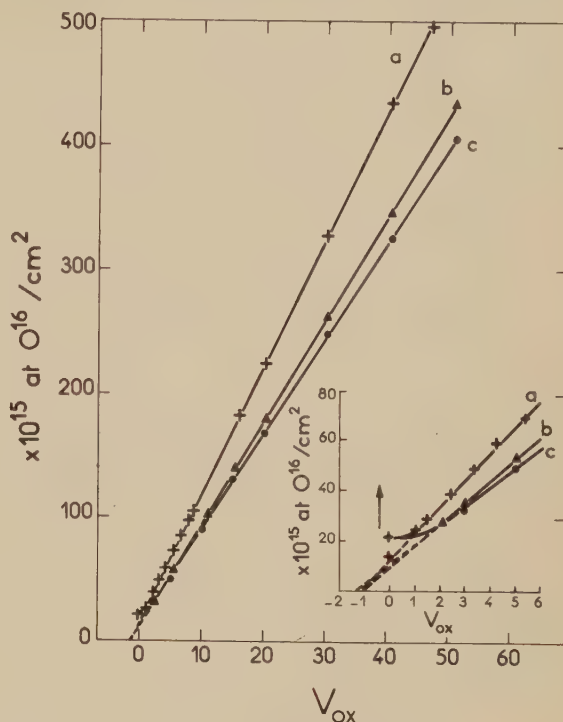


Fig. 1. $N_{O16} = f(V_{ox})$ for polished tantalum for various final current densities: curve a, of the order of 1 μ A/cm² (constant potential); curve b, 1 mA/cm²; curve c, 10 mA/cm². The insert shows the detail near the origin.

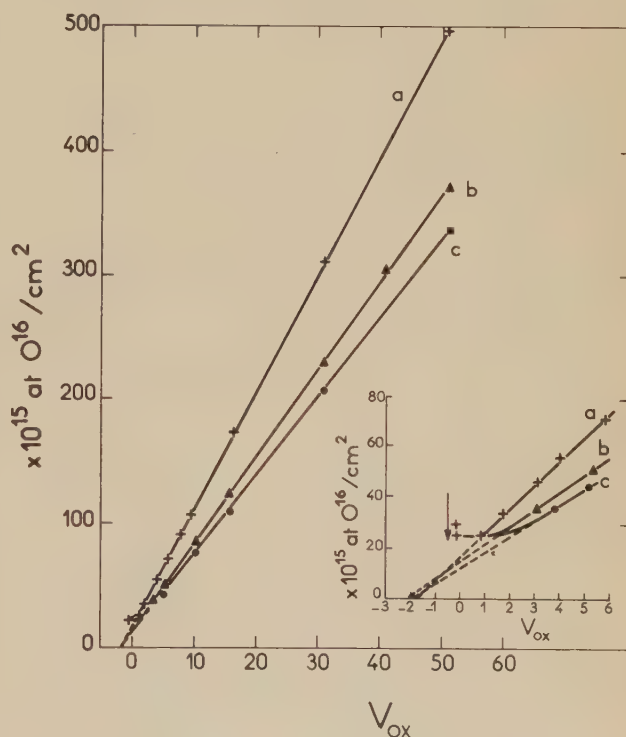


Fig. 2. $N_{O16} = f(V_{ox})$ for unpolished aluminum: curve a, below 10 μ A/cm² (constant potential); curve b, 1 mA/cm²; curve c, 10 mA/cm². The insert shows the detail near the origin.

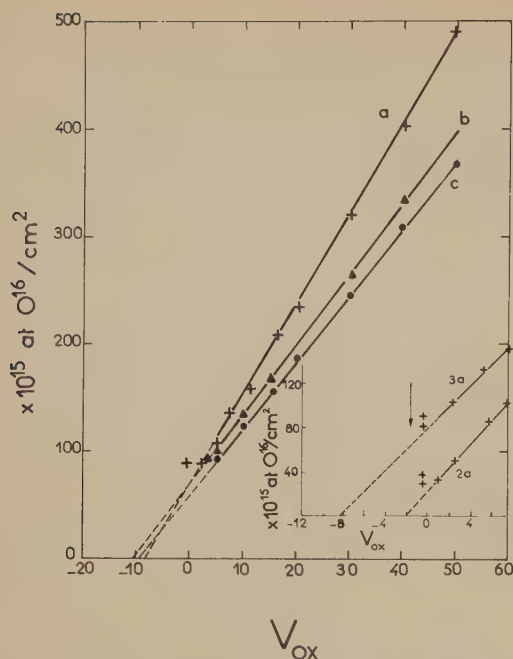


Fig. 3. $N_{O16} = f(V_{ox})$ for polished aluminum: curves a, b, c see Fig. 2. The insert compares in detail the growth laws at constant potential for unpolished (curve 2a) and polished aluminum (curve 3a).

change when the sample is immersed in the solution, before any potential is applied. This variation is shown in these figures (direction of the arrow).

The anode potential V_{ox} satisfies, according to Young (1), the relation

$$V_{ox} - V_{eq} = \eta_m + \eta_s + \eta_{ox} \quad [2a]$$

throughout the oxidation, where η_m is the overpotential at the metal-oxide interface, η_s that at the oxide-solution interface, and η_{ox} that in the oxide. V_{eq} is the anode equilibrium potential; this potential is equal to the thermodynamic potential V_{th} for the formation of the oxide (1-3) for which the over-all reaction can be written



where M represents the metal.

If all the oxygen on the sample surface is contained in a highly insulating oxide film which behaves as an anodic barrier layer, we may write

$$\eta_{ox} = \lambda E_{ox} N_O \quad [2b]$$

where E_{ox} is the electric field of formation of the oxide. If the film contains a region of high ionic conductivity, with oxygen content N_O^c , we have

$$\eta_{ox} = \lambda E_{ox} (N_O - N_O^c) \quad [2c]$$

Hence, in the most general case we have

$$V_{ox} - V_{eq} = [\eta_m + \eta_s - \lambda E_{ox} N_O^c] + \lambda E_{ox} N_O \quad [3b]$$

The intercept $V_{ox}(0)$ of the curve $N_O = f(V_{ox})$ with the V_{ox} axis for $N_O = 0$ is given for constant N_O^c by

$$V_{ox}(0) - V_{eq} = \eta_m + \eta_s - \lambda E_{ox} N_O^c \quad [3c]$$

It is clear from Eq. [3c] that in the case when an initial layer of high ionic conductivity is present on the sample surface, the curve $N_O = f(V_{ox})$ is shifted toward the negative potentials. Moreover, if $N_O^c = 0$ the curves $N_O = f(V_{ox})$ for various current densities (hence various E_{ox}) intersect at one and same point, the intercept $V_{ox}(0)$ yielding the sum of the overpotentials.

In order to determine with precision the values of the parameters of Eq. [3b] it is advantageous to operate in conditions such that the curves $N_O = f(V_{ox})$ are linear. In particular E_{ox} and the overpotentials should be constant; this was insured by taking into account the following considerations. The final current density J may be decomposed in the oxide according to

$$J = J_i + J_e \quad [4]$$

where J_i is the ionic and J_e the electronic current density, respectively. It is known that one to one relations exist between E_{ox} and J_i and between the overpotentials and J_i ; furthermore these relations are of the logarithmic type. Hence E_{ox} and the overpotentials are constant if J_i is, and are nearly constant even if J_i varies slightly, owing to their logarithmic dependence on the latter. In the case of oxidations at constant current ($1 \leq J \leq 10$ mA/cm²) J_e was always less than 5% of J (see below); this insures a good constancy of J_i by simply controlling J itself. In the case of oxidation at constant potential, at the low final current densities reached, J_e may be a large fraction of J . In this case we have no precise estimation of J_i and it appears that the control of the duration of the anodic treatment leads to a better constancy of J_i than the control of J , as illustrated by additional results below. Figures 1 to 3 clearly illustrate that operation according to these principles leads to the linear relations expected.

The experimental values of the slopes of the straight lines in Fig. 1, 2, and 3 and of the intercepts $V_{ox}(0)$ were determined by a method of least squares; they are listed in Table I. In our experimental conditions the thermodynamic potential V_{th} for the formation of tantalum oxide is equal to -1.15 V (30) and for the formation of hydrated aluminum oxide or anhydrous aluminum oxide to -1.9 and -1.84 V, respectively (31); over the whole range of currents investigated for polished tantalum and unpolished aluminum the values $V_{ox}(0)$ are very close to these theoretical values of V_{th} . The mean value of the difference with V_{th} is -30 mV for Ta_2O_5 , and -13 or -73 mV for Al_2O_3 ,

Table I. Characteristic constants of the growth laws

Metal	Surface preparation	J , mA/cm ²	$dN_O/dV_{ox} = \frac{1}{\lambda E_{ox}} \times 10^{15} \text{ at./cm}^2 \text{ V}$	$V_{ox}(0)$ deduced from	
				$N_O = f(V_{ox})^*$	$\hat{N}_{O16} = \hat{g}(V_{ox})$
Tantalum	Polished	10	8.20 ± 0.02	-1.20 ± 0.08	—
		1	8.79 ± 0.02	-1.15 ± 0.06	—
		$\sim 10^{-3}$	10.84 ± 0.08	-1.19 ± 0.05	$+0.63 \pm 0.1$
Aluminum	Unpolished	$\sim 10^{-3}$	10.52 ± 0.08	-2.13 ± 0.1	$+0.63 \pm 0.1$
		10	6.20 ± 0.03	-10.71 ± 0.2	—
	Polished	1	6.46 ± 0.02	-10.67 ± 0.12	—
		$< 10^{-2}$	7.96 ± 0.1	-8.3 ± 0.2	$+0.75 \pm 0.1$
	Unpolished	10	6.36 ± 0.03	-1.86 ± 0.17	—
		1	7.03 ± 0.03	-2.02 ± 0.12	—
		$< 10^{-2}$	9.26 ± 0.11	-1.86 ± 0.07	$+0.75 \pm 0.1$
	Thermally** oxidized	$< 10^{-2}$	9.26 ± 0.11	-1.80 ± 0.1	$+4.60 \pm 0.1$

All errors arise from the statistical spread of the nuclear countings and were calculated by the method of least squares.

* Compare with the values of the thermodynamic potentials V_{th} : -1.15 V for Ta_2O_5 and -1.84 V for Al_2O_3 .

** At 520°C, 3 hr in dry air.

with a statistical standard deviation of 80 and 170 mV, respectively. It can be deduced that the sum of the overpotentials $\eta_m + \eta_s$ is statistically zero with the standard deviation indicated. By contrast the straight lines corresponding to polished aluminum are considerably translated toward negative potentials with respect to those for unpolished aluminum, as is shown in detail on Fig. 3. Moreover the initial layer contains about three times more oxygen on polished aluminum than on unpolished aluminum. In view of Eq. [3c] this result strongly suggests that the anodic oxides on the polished aluminum samples contain a layer of high ionic conductivity; it seems likely that this layer originates in the initial oxide layer left on the samples after the polishing procedure.

It appears also that when the growth law curve is shifted toward negative potentials the corresponding slope decreases. In the case of aluminum the ratio of the slopes for polished and unpolished samples varies between 0.98 to 0.86 as the current density varies between 10 mA/cm² and some μ A/cm².

Control experiments carried out at constant potential, in electrolytes containing 0.5% by weight of salt (i.e., 10 times less than above), produced the same results as those of Fig. 1-5 and Table I, within experimental error. This shows that the influence of salt concentration on the growth laws is very small, if any.

Influence of the initial oxide layer.—In order to get further insight in the phenomena induced by the presence on the sample surface of the initial oxide layer arising either from the polishing or from the spontaneous oxidation of the metal the shape of the growth laws near the origin was studied in more detail both in natural and in O¹⁸-labeled solutions. As the shift of the curve $N_0 = f(V_{ox})$ toward negative potentials was observed on polished aluminum samples for which the initial layer contains a relatively high quantity of oxygen, the growth laws were further studied on samples covered by an initial layer of similar oxygen content but of different origin. Unpolished aluminum was hence thermally oxidized in air at 520°C for 3 hr and then further oxidized anodically at constant potential in natural solutions. Figure 4 and Table I show the corresponding results. The growth of the anodic film starts at a potential V_1 much higher for thermally oxidized samples; nevertheless in spite of the presence of an about three times thicker initial layer, the growth law $N_0 = f(V_{ox})$ shows no translation toward negative potentials.

Experiments in O¹⁸-labeled solutions may give additional information on the role of the initial layers. Let $N_{O18} = g(V_{ox})$ be the growth law obtained in such solutions. In order to compare directly $N_{O18} = g(V_{ox})$ to $N_0 = f(V_{ox})$, (obtained from unlabeled films) it is convenient to normalize the results to 100% enrichment of the electrolyte used. We shall call $\hat{N}_{O18} = \hat{g}(V_{ox})$ these normalized values. If the initial layer behaves like a barrier layer, and if, in addition, the oxygen atoms it contains remain in the film obtained after oxidation, undergoing no isotopic exchange (which, as we shall see, is the case), Eq. [3b] applies to N_{O18} with the following alteration

$$V_{ox} - V_{eq} = \eta_m + \eta_s + \lambda E_{ox} \hat{N}_{O18} + \lambda E_{ox} N_0^i \quad [3d]$$

for $V_{ox} > V_1$, where N_0^i is the oxygen content of the initial layer. It should be noted that the growth starting potential V_1 is equal to $\eta_m + \eta_s + \lambda E_{ox} N_0^i$ and hence slightly depends on J_i ; the experiments shown here were all made at constant potential, i.e., at low final current densities. Equation [3d] shows that the

straight line $\hat{N}_{O18} = \hat{g}(V_{ox})$ differs from $N_0 = f(V_{ox})$ only by a translation toward positive potentials. Any deviation from such a behavior indicates a more complicated role of the initial layer in the oxide growth than assumed.

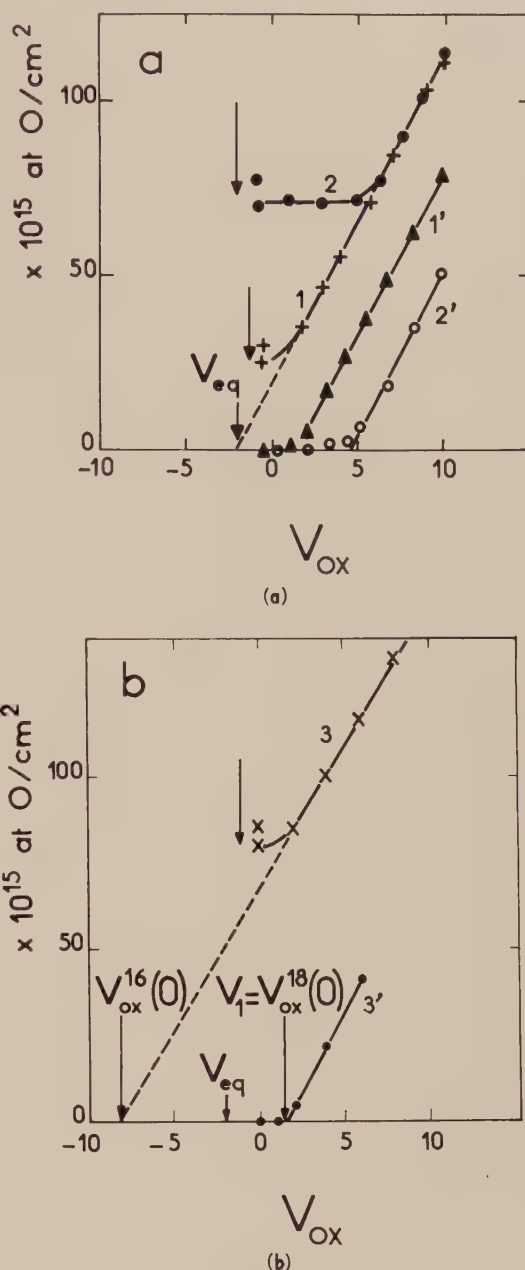


Fig. 4. Growth laws for aluminum at constant potential: (a) unpolished and (b) polished samples. Curves 1, 2, 3 represent $N_0 = f(V_{ox})$, respectively, for unpolished; unpolished and thermally oxidized; polished samples. Curves 1', 2', 3' represent $\hat{N}_{O18} = \hat{g}(V_{ox})$ for samples of the same type anodized in O¹⁸ enriched solutions.

Figure 4a shows $\hat{N}_{O18} = \hat{g}(V_{ox})$ for unpolished aluminum, both thermally oxidized and not. It is clear that these curves strictly obey Eq. [3d], V_1 increasing with the oxygen content of the initial layer. Figure 4b shows the corresponding results for polished aluminum. We see here that, in spite of the presence of a thick initial layer, the starting potential V_1 , as observed on $\hat{N}_{O18} = \hat{g}(V_{ox})$, remains small, near the value observed for unpolished aluminum.

The results of Fig. 4 and Table I suggest the following interpretation. The shift toward negative potentials of $N_{O18} = f(V_{ox})$ is not dependent on the oxygen content of the initial layer but on its nature. The initial layers of thermal origin behave like a barrier layer having no influence on the growth law and presenting no isotopic exchange of oxygen during further anodic oxidation, like anodic aluminum oxides, as shown in

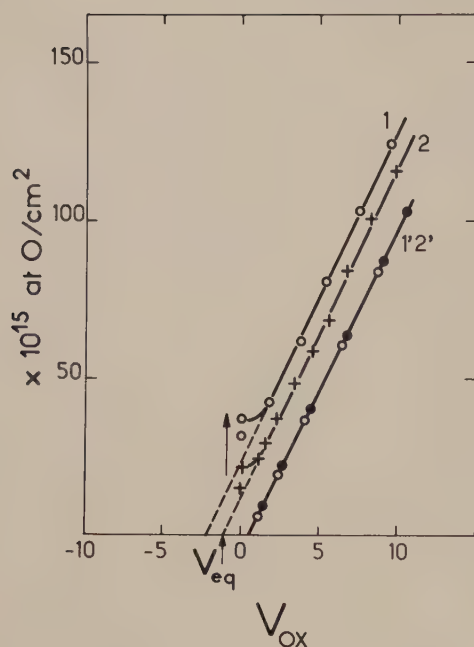


Fig. 5. Growth laws for tantalum at constant potential. $N_{O16} = f(V_{ox})$: curve 1, unpolished and curve 2, polished samples. $\hat{N}_{O18} = \hat{g}(V_{ox})$: curve 1', unpolished and curve 2', polished samples.

ref. (10). The initial layer on polished aluminum consists of two regions: (a) a region of high ionic conductivity responsible for the shift of $N_{O16} = f(V_{ox})$ by an amount $|V_{ox16}(0) - V_{eq}|$ and (b) a region of the barrier type responsible for the shift of $N_{O18} = g(V_{ox})$ by an amount $V_{ox18}(0) - V_{eq}$. This region has an oxygen content similar to that of the initial layer on the unpolished aluminum. The relative oxygen content of these regions is the ratio of these potential shifts, i.e., 2.6 in this case. Moreover the layer of high ionic conductivity does not undergo isotopic exchange of oxygen during anodic treatment. These results indicate that the oxygen coming from the solution merely passes through the layer of high ionic conductivity, if we assume that the latter remains at the oxide-solution interface; in this case this layer would have a porous character (see Discussion).

Figure 5 shows the growth laws obtained on polished and unpolished tantalum in labeled and unlabeled solutions, and Table I shows the corresponding parameters. A translation of the curve $N_{O16} = f(V_{ox})$ toward negative potentials for unpolished tantalum seems to indicate the presence of a layer of high ionic conductivity in this case. It should be noted that the curves $\hat{N}_{O18} = \hat{g}(V_{ox})$ have the same intercept with the potential axis for both types of tantalum used.

Electric field of formation.—The values of E_{ox} were deduced from the oxygen growth laws by assigning well chosen values to λ in Eq. [3b]. It should be noted that in order to obtain a linear relation $N_O = f(V_{ox})$,

when N_O^c is not vanishing, it is not necessary to require N_O^c to be a constant. In fact, if N_O^c itself varies linearly with V_{ox} , at least in a given range of potentials, the curve $N_O = f(V_{ox})$ remains linear. Such a behavior may change the value of the apparent field of formation E_{ox} as deduced from the slope of the curve $N_O = f(V_{ox})$. A decrease of N_O^c with V_{ox} may correspond to the gradual dissolution of an initial layer of high ionic conductivity or to pore-filling processes (32); an increase of N_O^c with V_{ox} may be caused by a partial formation of a hydroxide or of a porous layer during the anodic process (4). In the last case N_O^c may vanish at small V_{ox} , so that no shift of the intercept V_{ox} is observed. In what follows we shall calculate the apparent field E_{ox} ; the effects of the various behaviors of N_O^c will be considered in the Discussion.

For aluminum the roughness factor was taken equal to unity; this assumption will be discussed later. Like Young (1) and Diggle *et al.* (33) we assume that the barrier layers of aluminum oxide have the formula Al_2O_3 and are amorphous. The density of such layers was measured by several authors in various conditions; the reported values range from 2.73 g/cm³ (34) to 3.3 g/cm³ (35). Van Geel and Schelen (36) measured 3.1 g/cm³ for aqueous solutions; this value is near that of Bernard and Cook (5), 3.17 g/cm³, measured in organic solutions. This is in agreement with ref. (37) in which it is assumed that barrier layers formed in organic and aqueous solutions are similar from this point of view. Our calculations were based on the value 3.17 g/cm³.

For polished tantalum we shall take a roughness factor equal to unity in agreement with Young (1), who measured a density of 8.01 g/cm³ for aqueous solutions; this figure was later confirmed by Schrijner and Middelhoek (38) to within 0.5% precision. We admitted here a density of 8 g/cm³.

The calculated values of E_{ox} are listed in Table II. In order to compare our results to those of the literature, we also list in this table our values, recalculated with the densities used by the other authors quoted. For aluminum, E_{ox} is always larger on polished samples than on unpolished samples, the difference increasing with decreasing current density. Moreover our recalculated values on unpolished samples agree to within 2% with those of Harkness and Young (7), who did not use electrochemical polishing; our results on polished samples agree to within 5% with those of Bernard and Cook (5), who resorted to electrochemical polishing. These agreements might be fortuitous; nevertheless they are worthy to be noticed as Harkness and Young ascribed the difference between their values and those of Bernard and Cook to the influence of the different solutions used, whereas here the surface preparation seems to play a fundamental role. For tantalum there is excellent agreement with the values of Young (1) and good agreement for recalculated values with those of Vermilyea (39). The agreement with Young is natural for the values at high current density, as we too used coulometric measurements on tantalum to define our standard. At low current densities, where the faradaic efficiency might be less than 100%, the agreement is a good confirmation

Table II. Electric field of formation $E_{ox} \times 10^6$ V/cm

	J , mA/cm ²	Bernard and Cook (5) [$\rho = 3.17$]	Harkness and Young (7) [$\rho = 3.0$]	This work [$\rho = 3.17$]	
				Polished samples	Unpolished samples
Aluminum	10	9.62	8.44	9.1 (8.6)	8.8 (8.3)
	1	9.10	7.77	8.7 (8.2)	8.0 (7.6)
	$\leq 10^{-2}$	—	—	7.1 (6.7)	6.1 (5.8)
	J , mA/cm ²	Vermilyea (39) [$\rho = 8.74$]	Young (1) [$\rho = 8.0$]	This work [$\rho = 8.0$]	
				Polished samples	
	10	7.1	6.6	6.6 (7.2)	
Tantalum	1	6.5	6.2	6.2 (6.8)	
	$\sim 10^{-3}$	—	5.1*	5.0 (5.5)	

Values recalculated for the densities 3.0 g/cm³ and 8.74 g/cm³ for aluminum and tantalum respectively, are listed in brackets.

* For 1 μ A/cm².

of the value of Young, as our value, determined by nuclear microanalysis, is not influenced by the presence of an electronic current.

Components of the current.—The ionic current density in Eq. [4] may be in turn decomposed at the oxide-solution interface according to

$$J_i = J_{ox} + J_{dis} \quad [5]$$

where J_{ox} is the part of the current which contributes to the film growth and J_{dis} the dissolution current. J_{dis} includes the current density of direct dissolution of the cations as well as that equivalent to the dissolution of oxide already formed. The one to one empirical relation between J_i and E_{ox} may be written conveniently

$$J_i = A \exp B E_{ox} \quad [6]$$

where, for a given system A and B are temperature-dependent parameters. According to various authors (1, 40) B may slowly vary with E_{ox} , this leading for example to a quadratic term in the exponential. In what follows, at constant temperature and in the range of current densities covered, we shall consider B as constant and estimate its value from Eq. [6].

The components of J_{ox} and J_{dis} may be separated if J_i is known. This implies an estimation of J_e in Eq. [4], which might be carried out as shown below. J_{ox} is in fact given directly by the nuclear measurements. By definition the number $N_o(t)$ of oxygen atoms per square centimeter in the layer at time t is

$$N_o(t) - N_o(0) = k \int_0^t J_{ox}(\theta) d\theta \quad [7a]$$

$$= k \int_0^t R(\theta) J(\theta) d\theta \quad [7b]$$

where $R(t)$ is the oxidation current efficiency at any instant

$$R = \frac{J_{ox}}{J} \quad [8]$$

and where the constant k is equal to 0.312×10^{19} atoms of oxygen per coulomb, if we assume that the oxygen is fixed in the film in the state O^{--} .

For oxidations carried out at constant current, the precise measurement of the number Q of coulombs per square centimeter

$$Q = \int_0^t J(\theta) d\theta \quad [9]$$

consumed during oxidation allows the determination of the oxidation current efficiency from the following relation, deduced from [7b]

$$R = \frac{1}{k} \frac{dN_o}{dQ} \quad [10]$$

This quantity is easily measured and will be used to determine J_{ox} by using Eq. [8].

Measurements at constant current.—The oxidation of tantalum and aluminum at constant current (1 to 10 mA/cm²) in presence of a redox system yields an upper limit of the electronic component J_e : 1% of the current for polished Ta in agreement with ref. (9), 2% for polished Al, 5% for unpolished Al and Ta. By dif-

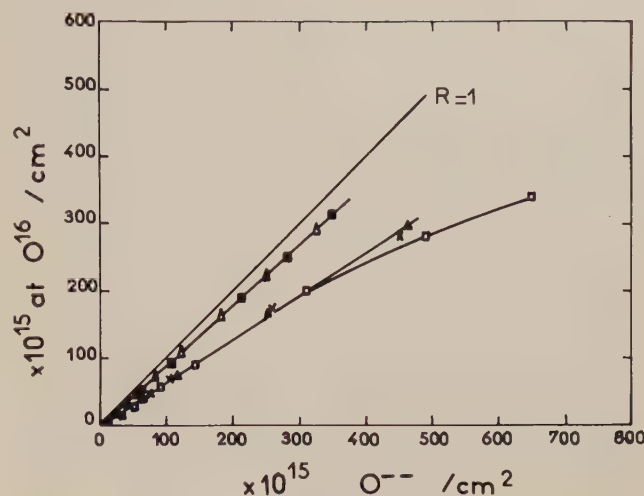


Fig. 6. Number of O^{16} atoms/cm² fixed on aluminum samples by anodic oxidation vs. electric charge consumed, expressed as a number of O^{--} anions/cm². Δ polished Al, 10 mA/cm² and $\blacksquare$ 1 mA/cm²; $\blacktriangle$ unpolished Al, 10 mA/cm², $\times$ 6.6 mA/cm², and $\square$ 1 mA/cm².

ference we obtain the minimum value of the ionic current density J_i . For each type of samples used it is thus possible to estimate the value of the constants A and B in the empiric relation [6]. The approximate values of A and B obtained, using the values of E_{ox} determined at 1 and 10 mA/cm² from Table II are listed in Table III. The agreements between our results and the literature are similar to those found in Table II.

On Fig. 6 the number of O^{16} atoms per square centimeter fixed on the surface of aluminum samples by anodic oxidation at constant current (minus the initial layer) is plotted as a function of the number of coulombs per square centimeter used during formation of the film (this quantity being expressed in numbers O^{--} /cm²). The slope of the curves gives, by definition, the values of R . Here $R = 1$ for tantalum and is not considered.

For polished aluminum the current efficiency is independent of the current. For unpolished aluminum the decrease of the efficiency as the layer thickness increases and the current density decreases, is due to an increase in the dissolution current, as the electronic current is less than 5% of the total. Moreover R is much smaller for unpolished than for polished aluminum. The various components of the current as deduced from the values of J_e and R are listed in Table IV. The large values of J_{dis} found for aluminum, especially for unpolished samples, raise the question whether the dissolution currents are of chemical or electrochemical nature.

The equivalent chemical dissolution current density for aluminum oxide was measured by nuclear methods, without applied electric field (this being in fact proportional to $-dN_o/dt$); an estimated value of only about $0.3 \mu\text{A/cm}^2$ for both polished and unpolished aluminum was found. It would therefore appear that the dissolution current during oxidation is purely electrochemical. This is in agreement with ref. (37). The dissolution current density on tantalum was not measurable, an estimated upper limit being 3×10^{-3}

Table III. Values of the constants A and B

	Literature	A (A/cm ²)	This work	Literature	B (10 ⁻⁶ cm/V)	This work
Aluminum	10 ⁻²⁶ to 10 ⁻²⁰ (5, 6) 10 ^{-14.6} (7)		10 ^{-25.7*} 10 ^{-13.8**}	4.4 to 5.5 (5, 6) 3.2 (7)		5.8* 2.9**
Tantalum	10 ⁻¹⁹ to 10 ⁻¹⁷ (1, 38)		10 ^{-17*}	5 to 5.5 (1, 38)		5.28*

* Polished samples.

** Unpolished samples.

Table IV. Components of the currents for aluminum at constant current densities

Surface preparation	V_{ox}, V	J_e , mA/cm ²	Expressed in % of J_e	Expressed in % of J_{J_1}	Expressed in % of J_{J_1}	Expressed in % of $J_{J_{1s}}$
Polished	0-50	$1 \leq J \leq 10$	≤ 2	98	92 ± 5	8
Unpolished	0-30	1	≤ 5	95	68 ± 4	32
		6.6	≤ 5	95	68 ± 4	32
		10	≤ 5	95	68 ± 4	32
	30-50	1	≤ 5	95	42 ± 3	58
		6.6	≤ 5	95	65 ± 5	35
		10	≤ 5	95	65 ± 5	35

The values of J_e and of J_{ox} were calculated directly from measurements; the value of J_1 and $J_{J_{1s}}$ were deduced by difference.

Measurements at constant potential.—These measurements were carried out at $V_{ox} = 50V$. At the low final current densities reached in this case the electronic current density J_e may be relatively high and the value of J_1 cannot be inferred from that of J . However, J_{ox} may be estimated directly from the relation (see Eq. [7a])

$$J_{ox} = \frac{1}{k} \frac{dN_o(t)}{dt} \quad [11]$$

We may in addition estimate J_1 at any instant t , by using Eq. [6], in which E_{ox} is deduced from Eq. [3b] by inserting $N_o(t)$ and where A and B are assumed to have the same values as at higher currents (Table III). This procedure implies that the nature of the films formed at low final currents is the same as at high constant current, i.e., that λ and N_o^c remain constant throughout the treatment. The values thus found should satisfy the inequality

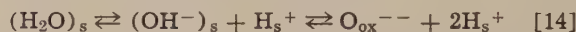
$$J_{ox} \leq J_1 \leq J \quad [12]$$

Violation of this equation would suggest that a film of different nature from the barrier layer is formed.

Results for oxidations for various durations are listed in Table V where the values for J_1 should be considered as orders of magnitude whereas the errors on J_{ox} are less than 50%. It appears that condition [12] is always satisfied, within experimental error, for the anodic oxidation of tantalum. Furthermore after 10-min oxidation the growth of the oxide is already slow and its rate tends toward zero for long periods, whereas the electronic current may represent more than 90% of the total. For the oxidation of unpolished aluminum it is only after 50 min that a current density J of less than $10 \mu A/cm^2$ is reached, the film continuing to grow slowly. With polished aluminum, on the other hand, the current density J decreases very rapidly and between 17 and 90 min J_{ox} is negligible. For both types of aluminum samples the inequality [12] is satisfied until 90 min. In this case the electronic current density may be estimated to represent about 90 and 60% of the total for polished and unpolished samples, respectively. Furthermore after 13 hr at constant po-

tential with both types of aluminum, J_{ox} is larger by orders of magnitude than the calculated J_1 and an appreciable growth of the oxide layer shows up. This may be ascribed to the formation of a layer of high ionic conductivity, i.e., an increase of N_o^c , which, if not taken into consideration, leads by the use of Eq. [3b] to too small values of E_{ox} . This interpretation is supported by the fact that after 60 hr under potential the films are of porous character, as proved by the stain test with an organic dye. Hunter and Towner (28) and Hoar and Yahalom (29) made similar observations.

Isotopic exchange of O^{18} .—The ionic transfer reactions at the oxide-solution interface leading to oxide formation may be written as (9, 41)



where the index "ox" stands for ions in the oxide, "s" in the solution. Reaction [13] describes cation transfer, the oxide being formed by precipitation; reaction [14] describes oxygen transfer. If at the interface there is only one type of reaction responsible for ionic transport, the classical theory of the overpotential can be applied (27, 41) relating the ionic current density J_1 during oxidation to the electrochemical exchange current J_{ex} for the reaction as follows

$$J_1 = J_{ex} \left[\exp \left(\frac{\alpha Z F}{RT} \right) \eta_s - \exp \left(- \frac{(1 - \alpha) Z F}{RT} \eta_s \right) \right] \quad [15]$$

where α , Z , F , R , and T have their usual meaning.

O^{18} tracing allows a direct determination of J_{ex} by observing the rate of isotopic exchange of oxygen between the oxide and the solution, no external field being applied. This rate depends both on J_{ex} and on the self-diffusion of oxygen in the oxide. The theory of these processes was developed in detail in papers published by our group (27, 41, 43). The slope of the curve $\hat{N}_{O18}(t)$ at the origin gives the values of J_{ex} independently from the oxygen self-diffusion rate.

Table V. Oxide growth during the constant potential phase

Metal	Time of oxidation*	$N_o(t)$, 10^{15} at./cm ²	J , $\mu A/cm^2$	J_1 , $\mu A/cm^2$ (calculated)	J_{ox} , $\mu A/cm^2$
Polished tantalum	0	406 ± 2	5000	5000	—
	10 min	530 ± 2	~ 1	~ 0.8	0.8
	50 min	536 ± 3	~ 1	~ 0.8	0.45
	13 hr	560 ± 3	~ 1	~ 0.1	0.1
	62 hr	600 ± 4	~ 1	~ 0.02	0.05
Unpolished aluminum	0	340 ± 2	5000	~ 5000	—
	10 min	435 ± 2	30	~ 20	12
	50 min	495 ± 3	10	~ 2	2
	90 min	500 ± 3	5	~ 2	0.2
	13 hr	641 ± 3	5	~ 0.04	0.4
	62 hr	2380 ± 10	10	$\sim 3 \times 10^{-5}$	1.6
Polished aluminum	0	385 ± 2	5000	~ 5000	—
	17 min	501.4 ± 3	5	~ 0.1	~ 0
	50 min	501.7 ± 3	2.5	~ 0.1	~ 0
	90 min	501.7 ± 3	1.8	~ 0.1	~ 0
	14 hr	615.5 ± 4	3.2	$\sim 10^{-4}$	0.5
	60 hr 30 min	2318 ± 10	5.1	$\sim 10^{-10}$	1.6

* After $V_{ox} = 50V$ is reached, at 5 mA/cm² current density.

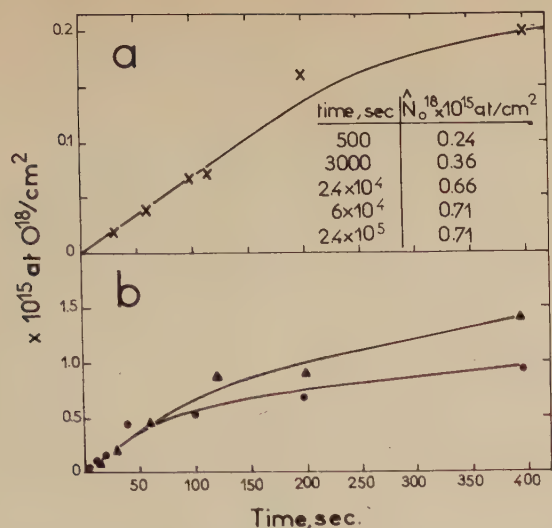


Fig. 7. Isotopic exchange in O^{18} enriched solutions as a function of time for oxides formed at 20V, 10 mA/cm² in O^{18} depleted solutions: a, tantalum; b, aluminum: $\blacktriangle$, unpolished; $\bullet$, polished samples.

The question arises whether under a high field, the growth of the anodic layer does in fact occur by transfer of oxygen at the oxide-solution interface. Comparison of the electrochemical exchange current J_{ex} of oxygen obtained by tracing with O^{18} , with the exchange currents calculated from Eq. [15] for various values of the ionic current allows the question to be elucidated. The experiments on isotopic exchange with no applied field were carried out on oxides initially formed at constant current (10 mA/cm²) up to 20V in O^{18} -depleted water. The samples were then immersed in a solution enriched in O^{18} for increasing lengths of time t . The results are shown in Fig. 7.

In the case of tantalum, after a linear start, the exchange slows down and the saturation is reached after about 6 hr. The saturation value, 7×10^{14} at./cm² suggests that the exchange is confined to the first (or first few) molecular layer. This was confirmed by slightly dissolving the oxide. After about 15Å of oxide have been removed the O^{18} has completely disappeared. The slow dissolution of the oxide was obtained in a solution of 300g NH_4F /liter of concentrated HF as in ref. (9), according to a procedure used by Pringle (42). At 27.5°C a uniform dissolution rate of 62 ± 3 Å/min was observed (9, 43) in our experimental conditions. It must be verified that the observed phenomenon was not due to simple spontaneous growth of an oxide film in the enriched solution. The sample which had undergone isotopic exchange to saturation was hence immersed again in the depleted solution. The observed disappearance of O^{18} after several hours, which cannot be due to dissolution (as seen above), proved the reversibility of the phenomenon, characteristic of isotopic exchange. The observed saturation indicates a very low diffusion coefficient of oxygen in the oxide Ta_2O_5 , in agreement with (43). The slope at the origin of the curve in Fig. 7a yields a value of the exchange current density of $0.3 \mu\text{A/cm}^2$, with 15% precision.

Analogous results were obtained for aluminum for times below 10 min (Fig. 7b). For times of the order of an hour the O^{18} uptake goes on increasing slowly.

Thus after 63 hr we found on polished and nonpolished samples, respectively, 15×10^{15} and 16×10^{15} at./cm². On the other hand a loss of the initial oxygen content of 62 and 69%, respectively, was observed, in agreement with the value of the dissolution current found above. The absence of a saturation effect on aluminum may be due to the corrosive attack of the solution; a high self-diffusion rate of oxygen in the barrier layer is unlikely taking into account the results of ref. (10). The slopes at the origin of the curves in Fig. 7b yield a value of the exchange current density of $3 \mu\text{A/cm}^2$ with 30% precision.

From Eq. [15], using the experimental values of the overpotentials and of J_i , an order of magnitude of the electrochemical exchange current density of OH^- anions was deduced. As the sum of the overpotentials is statistically zero, we took for $\eta_m + \eta_s$ the corresponding standard deviations; this leads to lower limits for J_{ex} . These values and the results from the exchange experiments are listed in Table VI. The complete disagreement between the corresponding values of J_{ex} will be interpreted in the Discussion.

Discussion

Initial layers on aluminum samples.—The existence of an oxide layer of high ionic conductivity on the surface of polished aluminum samples clearly appears from the above results. Its presence and nature may account for some of the differences in the behavior of polished and unpolished aluminum during anodic oxidation, in particular the observed decrease of the slope dN_O/dV_{ox} , on polished samples. A first explanation could be that this layer is an insoluble oxygen containing residue from the polishing bath. Preliminary experiments similar to that of ref. (10), using the $Al^{27}(p,\gamma)Si^{28}$ resonant reaction, indicate however that this layer has a high aluminum content. It seems therefore that the layer is a porous aluminum oxide film or perhaps a hydroxide; the use of O^{18} tracing and the localization of the O^{18} after various anodic treatments of the metal will give further insight in the nature of this film and in the mechanism of its influence on the anodic oxide formation. This conclusion may be related to the results of Hollo (16) who found by electron microscopy that electropolishing in a phosphoric acid-butyl alcohol bath yields a porous oxide film and to those of Welsh (44) who found similar results using various electropolishing baths.

Dependence of the oxygen growth law slopes on sample preparation.—The higher values of the slopes dN_O/dV_{ox} for unpolished than for polished aluminum could be explained by a corresponding difference in the roughness factor of the metal under the oxide. Under this assumption the difference would depend on the final oxidation current density J , and would be maximum for J equal to some $\mu\text{A/cm}^2$. Now, this value was reached after a stage at high current (5 mA/cm^2) at the end of which the slopes are not significantly different (Table I); hence neither are the roughness factors. It is difficult to imagine a mechanism which would lead to an increase in roughness factor during a phase at constant potential and low current. Hence we shall admit that the roughness factor of the metal backing was near unity.

Two possible explanations will now be considered:

(i) The anodic films formed on both polished and unpolished aluminum are pure Al_2O_3 oxides. The

Table VI. Oxygen exchange currents

Metal	$\eta_m + \eta_s$, mV	J , $\mu\text{A/cm}^2$	J_i , $\mu\text{A/cm}^2$	Minimal values of J_{ex} calculated from Eq. [15], $\mu\text{A/cm}^2$	J_{ex} deduced di- rectly from the isotopic exchange of O^{18} , $\mu\text{A/cm}^2$
Polished tantalum	0 ± 80	10^4	$\sim 10^4$	2×10^3	0.3 ± 0.05
Both polished and un- polished aluminum	0 ± 170	10^4	9.5×10^3	3×10^2	3 ± 1

smaller slope on polished aluminum would be due to the superposition of this oxidation mechanism and of the slow transformation of a part of the layer of high ionic conductivity initially present at the surface into a barrier layer. The growth law corresponding to unpolished aluminum would then be characteristic of barrier layer formation alone, (i.e., yield the real E_{ox}). Similar assumptions may hold for tantalum. In the case of aluminum the transformation of the high ionic conductivity layer may be due to two types of mechanisms: those which do not lead to an increase of its oxygen content [for example, the transformation of $Al(OH)_3$ into Al_2O_3 by proton repulsion] and those which do (i.e., pore filling process).

(ii) The growth law characteristic of barrier layer formation alone would correspond, according to this assumption, to polished aluminum. The higher slope for unpolished aluminum (i.e., a lower apparent E_{ox}) would be due here to the simultaneous formation of a barrier layer and of a layer of high ionic conductivity (hydroxide or porous film). The ratio of the slopes would correspond then to the proportion of oxygen present in the barrier layer with respect to the total amount of oxygen in the film formed on unpolished aluminum. Polishing would appear as preventing such phenomena, the layer of high ionic conductivity remaining unchanged during treatment. This assumption cannot be applied to tantalum.

The real phenomenon could be a combination of these two mechanisms. In particular the second mechanism could play an increasing role with decreasing current densities as indicated by the porous oxidation phenomena which appear at low current densities. In any case the ratio of the slopes being close to unity, the proportion of the current J_{ox} which may contribute to the transformations of type (i) or (ii) is small.

Ion transfer at the oxide-solution interface.—The large value of the electrochemical dissolution current J_{dis} for aluminum in our solution indicates a considerable mobility of the cations at the oxide-solution interface. This is confirmed by the observations of Davies *et al.* (37) who directly determined the presence of the aluminum cations in the ammonium citrate solution. The relative values of J_{dis} with respect to J found by these authors on electrochemically polished aluminum differ from our results; in particular they found that this ratio depends on J , whereas no such dependence appears in Fig. 6. This discrepancy may be due to the different polishing procedure used and to the much higher potential V_{ox} applied (120V as compared to 50V in our case). It should be noted that these phenomena depend strongly on the solution used; in particular J_{dis} is negligible in organic solutions of the type used by Vermilyea (45).

The discrepancy by several orders of magnitude between the values of J_{ex} directly measured by isotopic exchange of oxygen without any applied field for both aluminum and tantalum and the values deduced from Eq. [15], as listed in Table VI, may be interpreted in the following way. We may define a cationic transfer current J_c at the oxide-solution interface by the relation

$$J_c = J_{dis} + \theta J_{ox}$$

where θ represents the proportion of the oxidation current J_{ox} due to cation transfer. The oxygen transfer current is hence $(1 - \theta)J_{ox}$. In what follows we shall try to estimate the values of θ .

(i) The large difference between the measured and calculated values of J_{ex} may be explained in two ways:

1. The two experiments are not comparable and the electrochemical exchange current of oxygen may be much greater during anodic growth than without an applied field. According to the literature (46) we can assume that the electric field will have the effect of creating oxygen vacancies which will appear at the oxide-solution interface. The presence of these oxygen vacancies will then increase the transfer current of

oxygen at the interface which leads to a strong increase in the apparent electrochemical exchange current density of oxygen. This would explain the low values of the observed overpotentials and lead to $\theta \simeq 0$.

2. The low value observed for the overpotential in anodic growth may be explained by the transfer of cations predominating at the oxide-solution interface, ($\theta \simeq 1$). The chemical reaction in the double layer would be followed by precipitation thus contributing to film growth. Using relation [15] we may calculate in this hypothesis the apparent exchange current density J_{ex} for the transfer of Ta^{5+} or Al^{3+} cations. Taking $J_1 = J_c = 10 \text{ mA/cm}^2$ and $\eta = 0.1V$ we get the minimal values of J_{ex} equal, respectively, to 0.45 and $24 \mu A/cm^2$.

In the case of tantalum the high value of the cationic exchange current density calculated for $\theta = 1$ seems incompatible with the high chemical stability of the oxide, as well as with the observed absence of any dissolution current (Table V).

On the other hand the assumption $\theta = 1$ implies that the layer of high ionic conductivity present on polished aluminum samples should be rapidly buried in the oxide formed. If this layer is porous most of the current J_{ox} should contribute to its transformation into a barrier layer by pore filling; as seen above, this is not the case. If this layer is not porous, it should remain in contact with the metal; such a process seems unlikely. A definite conclusion may be reached only by localizing the final position of the initial layer by O^{18} tracing, an experiment which is in progress. All these considerations would appear to support the interpretation which implies that the growth of the oxide is achieved essentially by oxygen transfer at the oxide-solution interface, both for tantalum and aluminum. (ii) The fact that the oxidation is chiefly due to oxygen transfer does not imply that J_c is small but only that $J_c = J_{dis}$. For aluminum the cationic transfer current density may hence be very large, up to 60% of the ionic current (Table IV) and there is no contradiction between our conclusions. The small probability of the oxide forming reaction by cation transfer might be explained by the decrease of the free energy of the cations in the oxide with respect to that in the metal, as suggested by Novakovski and Likhachev (47) in the case of iron passivity phenomena.

It should be emphasized that the fact that the growth of the oxide is mainly due to oxygen transfer at the oxide-solution interface does not imply that oxygen transport takes place in the bulk of the oxide. In fact cations migrating through the oxide, on arriving near the interface, would also create oxygen vacancies, leading to the oxidation reaction. The discussion of ion transport phenomena in the bulk of the oxide is beyond the scope of this work.

Acknowledgment

The authors wish to thank Dr. C. Cherki and Dr. G. Feuillade for enlightening discussions. They are grateful to Professor D. Samuel and Dr. S. Szapiro from the Weizmann Institute for advice in the handling of labeled water. The help of E. d'Artemare for the operation of the Van de Graaff Accelerator has been much appreciated. This work was supported by the Centre National de la Recherche Scientifique, (RCP No. 157), the DRME, and the DGRST.

Manuscript submitted July 9, 1970; revised manuscript received Dec. 1, 1970. This was Paper 12 presented at the New York Meeting of the Society, May 4-9, 1969.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1971 JOURNAL.

REFERENCES

1. L. Young, "Anodic Oxide Films," Academic Press, New York (1961).
2. D. A. Vermilyea, "Anodic Films," Chap. IV, in

- "Advances in Elec. and Electrochemical Engineering," Vol. 3, Interscience Publishers Inc., New York (1965).
3. T. P. Hoar, "The Anodic Behaviour of Metals," Chap. IV, in "Modern Aspects of Electrochemistry," Vol. 2, Butterworth Scientific Publications, New York (1959).
 4. A. J. Brock and G. C. Wood, *Electrochim. Acta*, **12**, 395 (1967).
 5. W. J. Bernard and J. W. Cook, *This Journal*, **106**, 643 (1959).
 6. J. P. Ryan, Thesis, Toronto (1964).
 7. A. C. Harkness and L. Young, *Can. J. Chem.*, **44**, 2409 (1966).
 8. R. M. Goldstein and R. J. Lederich, *Thin Solid Films*, **5**, R 11 (1970).
 9. G. Amsel, C. Cherki, G. Feuillade, and J. P. Nadai, *J. Phys. Chem. Solids*, **30**, 2117 (1969).
 10. G. Amsel and D. Samuel, *ibid.*, **23**, 1707 (1962).
 11. G. Amsel, C. Cherki, J. P. Nadai, and J. Siejka, Paper 12 presented at the New York Meeting of the Society, May 4-9, 1969.
 12. G. Amsel and M. Croset, Paper 13 presented at the New York Meeting of the Society, May 4-9, 1969.
 13. G. Amsel, L. A. L. Report, 1053, Orsay (1963).
 14. G. Amsel and D. Samuel, *Anal. Chem.*, **39**, 1689 (1967).
 15. J. P. Nadai, Thesis, Orsay (1967).
 16. M. Gy. Hollo, *Acta Met.*, **8**, 265 (1960).
 17. C. G. Dunn and L. A. Harris, *This Journal*, **117**, 81 (1970).
 18. L. Holland, "Vacuum Deposition of Thin Films," p. 71, Chapman and Hall, London (1956).
 19. H. P. Godard, "The Corrosion of Light Metals," John Wiley & Sons, Inc., New York (1967); H. P. Godard and E. G. Torrible, *Corrosion Sci.*, **10**, 135 (1970).
 20. G. Amsel, D. Dieumegard, and B. Maurel, To be published.
 21. M. Croset, *Rev. Sci. Instr.*, **37**, 123 (1966).
 22. G. Amsel, *Ann. Phys.*, **9**, 297 (1964).
 23. S. Szapiro, Thesis, Rehovot, Israel (1965).
 24. I. Dostrovsky and D. R. Llewellyn, *J. Soc. Chem. Industry (London)*, **68**, 208 (1949).
 25. C. Ortega, J. Siejka, and G. Amsel, To be published.
 26. D. Samuel, Private communication.
 27. G. Feuillade and R. Jacoud, *Electrochim. Acta*, **14**, 1297 (1969).
 28. M. S. Hunter and P. F. Towner, *This Journal*, **108**, 139 (1961).
 29. T. P. Hoar and J. Yahalom, *ibid.*, **110**, 614 (1963).
 30. W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., Englewood Cliffs, New Jersey (1959).
 31. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, New York (1966).
 32. A. Dekker and A. Middelhoek, *This Journal*, **117**, 440 (1970).
 33. J. W. Diggle, T. C. Downie, and C. W. Goulding, *Chem. Rev.*, **69**, 365 (1969).
 34. G. A. Dorsey, *This Journal*, **116**, 466 (1969).
 35. W. G. Burgheers, A. Claassen, and J. Zernike, *Z. Phys.*, **74**, 593 (1932).
 36. W. Ch. Van Geel and B. J. J. Schelen, *Philips Res. Rept.*, **12**, 240 (1957).
 37. J. A. Davies, B. Domeij, J. P. S. Pringle, and F. Brown, *This Journal*, **112**, 675 (1965).
 38. A. J. Schrijner and A. Middelhoek, *ibid.*, **111**, 1167 (1964).
 39. D. A. Vermilyea, *Acta Met.*, **1**, 282 (1953).
 40. R. J. Dreiner and T. B. Tripp, *This Journal*, **117**, 858 (1970).
 41. G. Feuillade, *Electrochim. Acta*, **14**, 317 (1969).
 42. J. P. S. Pringle, This was Paper 11 presented at the New York Meeting of the Society, May 4-9, 1969.
 43. C. Cherki, Thesis, Paris, 1969.
 44. N. C. Welsh, *J. Inst. Metals*, **85**, 129 (1956-1957).
 45. D. A. Vermilyea, *Acta Met.*, **2**, 482 (1954).
 46. L. Young, W. S. Goruk, and F. G. R. Zobel "Oxide Films," in "Modern Aspects of Electrochemistry," Vol. 4, Plenum Press, New York (1966).
 47. V. M. Novakovsky and Y. A. Likhachev, *Electrochim. Acta*, **12**, 267 (1967).



An O^{18} Study of the Source of Oxygen in the Anodic Oxidation of Silicon and Tantalum in Some Organic Solvents

M. Croset

Centre de recherches SESCOSEM, Corbeville par Orsay-91-France

and E. Petreanu and D. Samuel

Isotope Department, The Weizmann Institute of Science, Rehovot, Israel

and G. Amsel and J. P. Nadai

Groupe de Physique des Solides de l'Ecole Normale Supérieure, Tour 23; 9, quai Saint-Bernard, Paris 5e, France

ABSTRACT

The anodic oxidation of silicon and tantalum in organic solvents containing small quantities of dissolved salts (KNO_2 and KNO_3) and water has been studied. The source of oxygen in the oxide layer has been determined using O^{18} -labeled materials. The isotopic exchange of oxygen between the various components of the electrolyte under thermal and electrolytically induced conditions was measured using mass spectrometric analysis and found to be extremely slow. Nuclear methods of analysis of isotopic oxygen were used to determine the source of oxygen in the oxide layer on both metals. It was found that over 80% of the oxygen of the oxide comes from water, the rest from the salt. The small extent of incorporation of nitrogen-containing anions in the oxide layers was also measured by a nuclear method.

A detailed study of the anodic oxidation of silicon has been undertaken in order to elucidate the phenomena occurring both in the electrolyte and in the growing oxide film. These phenomena have already received considerable attention in the literature and were first studied in 1957 in N-methylacetamide¹ solutions of KNO_3 and other salts by Schmidt and Michel (1). Since then, Duffek *et al.* have studied this process both in NMA (2) and in glycol (3) for various salt and water concentrations. In addition to the classical methods of investigation used by these authors we have resorted to a special technique developed to study anodic oxidation, i.e., microanalysis by means of nuclear reactions (4-7). The latter enables the precise determination of the oxygen content of oxide films and the investigation of the mechanisms of formation using O^{18} as a tracer.

Our study was aimed primarily at determining the source of the oxygen contained in the films. This can be the solvent, the salt, or traces of water in the solution, or a combination of these. Either NMA or glycol were used as solvents, containing small quantities of KNO_3 and water. For some experiments in glycol, KNO_2 was used. Either the water or the KNO_3 used were labeled with O^{18} .

Key words: anodic oxidation, silicon, tantalum, oxygen source, O^{18} tracing, isotopic exchange, organic solution, water, salt.

¹ In what follows, the abbreviation NMA will be used for N-methylacetamide.

In addition to the anodic oxidation of silicon, the same process on tantalum was also studied in order to investigate the similarities and differences in behavior of the two metals. The reasons for using tantalum are its ready oxidation in the above electrolytes, the high current efficiency of the oxidation process, and low field of formation as compared to silicon.

Once the source of the oxygen in anodic oxidation has been determined, the mechanisms of ionic transport in the films can be elucidated. This will be the subject of a further paper, although preliminary results on field-induced self-diffusion in anodic silicon oxide has been published recently (6). The aim of the present work was also to help in determining the optimal conditions of oxide film formation so as to make anodic oxide film production competitive with thermal growth methods.

Experimental

Preparation of samples to be oxidized.—Samples of p-type silicon were used, with a resistivity of about 0.1 ohm·cm. The surface of the silicon wafers polished by a mechano-chemical process, was cleaned before oxidation using classical methods: degreasing with trichloroethylene, rinsing, removal of the oxide layers with hydrofluoric acid, and finally rinsing with hot water (of resistivity greater than 15 megohm·cm) and air drying. The tantalum samples were cut from 0.2 mm thick rolled sheets with a highly polished surface,

supplied by Fansteel Corporation, with a stated purity 99.9%. The tantalum samples were cleaned with trichloroethylene, washed with methanol, and air dried.

Preparation of labeled compounds.— O^{18} -enriched water from the Isotope Separation Plant of the Weizmann Institute was used. This water, obtained by fractional distillation, is also highly enriched in deuterium. In order to eliminate both chemical and nuclear isotope effects this water was "normalized" so as to contain less than 0.1% deuterium by the method of Zhavoronkov [see ref. (8), p. 38]. In all cases, the water was purified by distillation first from permanganate and then under reduced pressure in silica vessels. For the anodic oxidation experiments the water used had the approximate isotopic concentration 88% O^{18} , 0.5% O^{17} , 11.5% O^{16} . Various high O^{18} concentrations were used for exchange experiments.

O^{18} -labeled potassium nitrate was prepared by acid catalyzed exchange with water, by the method of Anbar *et al.* (9), and contained 77% O^{18} . The salt used was shown to be free of any O^{18} -labeled water by dissolving it in the minimum quantity of water depleted in O^{18} [i.e., containing 0.007 a/o (atom per cent) oxygen- 18 , thirty times less than natural abundance]. On distilling the water and analyzing it for O^{18} , it was found to be unchanged in isotopic content.

In certain experiments made in order to examine the effect and quantity of residual water in "dry" solvents, "washed NMA" and "washed glycol" were prepared. In each case ca. 2 ml highly enriched H_2O^{18} was added to ca. 50g organic solvent of the best quality available and the solvent dried by repeated fractional distillation, the final product having a water content of less than 0.05%.

Preparation of organic solutions.—Most of the solutions used contained 0.4% water and 0.4% salt by weight. This salt content insures that the solution has a resistivity (which appeared to be independent of the water content) convenient for easy oxidation. In addition, preliminary studies showed that the optimal water content for the formation of high-quality silicon oxide films for semiconductor devices is in the vicinity of 0.4%.

When isotopically enriched materials were used, the weight of labeled components was increased in proportion to their molecular weight, so as to insure that the same number of molecules were present in both labeled and unlabeled solutions.

In all NMA solutions KNO_3 was used. However, difficulties were encountered in oxidizing tantalum in glycol using KNO_3 , when the water content was less than 2%. In particular, it was impossible to reach high anodic voltages, since breakdown occurred at about 20V. These difficulties could be overcome by using KNO_2 , as was done in a number of experiments with glycol solutions.

The solvents used (NMA from Eastman Kodak and glycol from Merck) were purified by double fractional distillation at reduced pressure through a column of molecular sieves. NMA was distilled at $60^\circ \pm 0.5^\circ C$, and glycol at $55^\circ \pm 0.5^\circ C$. The final product, containing less than 0.02% by weight of water (see later), was distilled directly into the electrolytic cell. The KNO_3 was dried on a vacuum line at $100^\circ C$ for 24 hr; the less stable KNO_2 *in vacuo* at room temperature for several days.

It should be noted that very small traces of impurities such as fluorides may have a deleterious effect on the anodic oxidation of silicon. These trace contaminants are not removed by the purification processes described above, so that certain batches of solvents had to be rejected, especially in the case of glycol.

Electrolyte solutions containing known quantities of O^{18} -labeled water had to be prepared with great care, since any water accidentally introduced will immediately dilute the isotopic content of the enriched water.

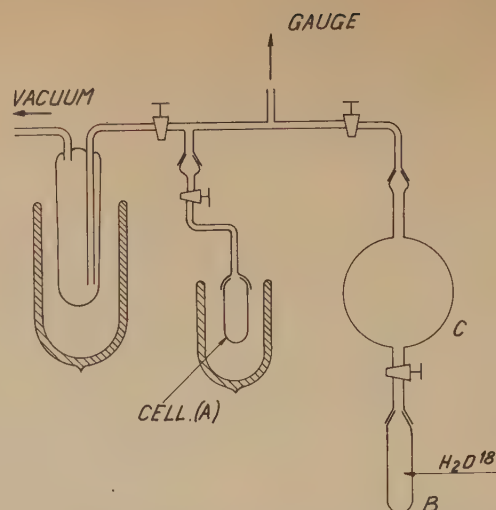


Fig. 1. Vacuum line used for transfer of O^{18} labeled water. A is electrolysis cell; B, H_2O^{18} reservoir, C, bulb for determining the quantity of water.

This could happen easily, since the solvents used were found to be very hygroscopic. It was, therefore, essential to transfer all distillable liquids on the vacuum line shown in Fig. 1. The dried, weighed salt (KNO_3 or KNO_2) is placed at the bottom of an electrolytic cell (A), which is then filled first with ca. 30 ml of "dry" solvent by distillation. The solvent is then carefully degassed and a given quantity of labeled water (determined by the volume of the bulb C and the saturation pressure of water at the temperature of the reservoir B maintained at $26^\circ C$) is transferred from the reservoir (B) to (A) by cooling the latter in liquid nitrogen. To prevent condensation of water vapor on other surfaces, the entire apparatus is kept at about $28^\circ C$. This enables the transfer of 60 mg of ordinary water (or its labeled equivalent) in each operation; the desired water content being obtained by repeating the above operation as many times as necessary. The problem of residual water in the solvent will be discussed later. The cell is then filled with dry argon, the cathode and samples to be oxidized are placed in position in a dry box, and the cell is ready for use.

For solutions of natural isotopic oxygen composition or for those containing an O^{18} -labeled salt, water was simply added using a microsyringe. In all cases, the total quantity of water in the electrolyte was determined just before oxidation as described below.

Method of oxidation.—The samples to be oxidized were placed as anodes opposite a platinum cathode. The solution was stirred magnetically and its temperature controlled by a thermostat. The Pyrex oxidation cell is sealed with a cover fitted with a spherical ground glass joint which supports the leads to the electrodes. Seven electrodes were placed in each cell so that successive oxidation of six samples could be performed without opening it (Fig. 2). Condensation of liquids on the walls of the cells was prevented by heating those parts not in contact with the bath.

Owing to the problems associated with maintaining electrical contact with silicon and tantalum foils, some details of the electrical connections will be given. In electrolytes where tantalum is easily oxidized (NMA + KNO_3 ; glycol + KNO_2) a special tantalum clamp, previously oxidized to 300V is used [see ref. (10)] with the sample totally immersed in the liquid. When glycol and KNO_3 is used to oxidize silicon, the clamp is kept above the surface of the liquid.

Oxidation was performed at a constant current of 1 mA/cm^2 up to a predetermined voltage (of up to several hundred volts), followed by a stage at constant voltage. The final current was allowed to decrease down to about $10 \mu\text{A/cm}^2$ for all samples. The duration of this stage varied from 2 to 4 hr for silicon and 10

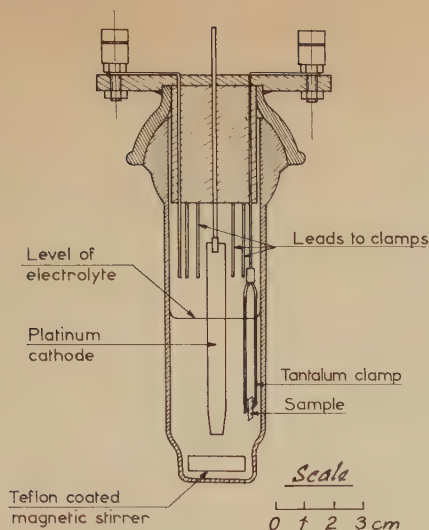


Fig. 2. Single compartment cell for successive oxidation of six samples without opening.

to 15 min for tantalum. The temperature of the solutions was maintained at about 20°C for glycol and, to avoid solidification, at around 35°C for NMA. After oxidation the samples were rinsed at 20°C in acetone, alcohol, and finally high resistivity water.

Under these conditions the thickness of SiO_2 films was measured by optical and nuclear methods and found to be about 6 Å/V, and that of Ta_2O_5 films about 16 Å/V. No gas evolution was observed at the anode during oxidation of either silicon or tantalum (see Discussion).

It was found that after a number of oxidations of silicon in glycol or NMA (consuming more than 1000 coulombs), further silicon samples cannot be oxidized satisfactorily. The solution apparently becomes poisoned by unknown decomposition products. For this reason the solutions, both isotopically labeled and unlabeled, were renewed frequently.

Exchange experiments.—Thermal isotopic exchange of oxygen between O^{18} -labeled water and glycol (or NMA) with or without added KNO_3 was examined. Various mixtures of the components of the system were heated in a sealed Pyrex tube in an oil or water bath for given times. In some cases the nitrate was labeled with O^{18} . The components were then separated and analyzed for their isotopic content, as described below.

The experiments on exchange during electrolysis were conducted at room temperature in a classical three-compartment cell with platinum electrodes. The cell consists of two electrode compartments (20 ml) and a middle compartment (15 ml), separated by sintered glass of porosity No. 1 (100 to 150 μ pores). Each compartment was stirred by means of Teflon-coated bar magnets and the temperature measured by a separate thermometer. After a given number of coulombs (usually 1000) had been passed through the cell, the components of the electrolyte were separated and analyzed for their isotopic content as described below.

Chemical analysis of the solutions.—Water was determined by the Karl Fischer method. Great care was taken during the transfer of the liquids for analysis: all manipulations were done in a dry box, using oven-dried syringes and injecting the sample directly into the titration chamber through a rubber stopper. The analysis was done by back-titration. Using these precautions, the limiting sensitivity was about 0.02% (by weight) of water in NMA or glycol; reproducibility was of the same order of magnitude.

The formation of nitrite in the nitrate solutions was determined by means of the Greiss reagent. The chem-

ical identification and analysis of other decomposition products was not attempted.

Isotopic analysis of the constituents of the solutions.—**Separation of labeled compounds.**—Water was removed from mixed solvents (from both exchange and electrolysis experiments) by distillation at atmospheric pressure using a 30 cm Vigreux fractionating column. The water was then redistilled in a micro still. Only when the NMA contained more than 2 ml water per 30g solvent could sufficient water of high purity for isotopic analysis be obtained. It was more difficult to isolate water from glycol, due to the formation of an azeotrope.

The organic solvent was then fractionally distilled (NMA at 80°C/4 mm; glycol at 65°C/10 mm). In order to eliminate the effect of traces of highly enriched O^{18} water in the isotopic analysis, a small quantity of unlabeled water was deliberately added to the distilled solvent and then removed by another distillation as described above. This procedure was repeated twice and the NMA or glycol dried with molecular sieves. Owing to the slow rate of isotopic exchange between NMA or glycol and water at room temperature, this procedure does not affect the isotopic content of the organic solvent at the low O^{18} concentrations found. Traces of residual water (<1%) do not affect the analysis of these isotopic concentrations.

The KNO_3 remains as a solid residue from the first fractional distillation. For the thermal exchange experiments, the heating of KNO_3 during distillation has only a negligible effect as compared to the previous much more drastic heat treatment. For the exchange during electrolysis the results on thermal exchange show that the effects of our distillation procedure was also negligible. To eliminate traces of H_2O^{18} in the salt the latter was washed and recrystallized twice with water. It was known that there is negligible isotopic exchange of oxygen under these conditions. It should be noted that recent experiments (7) using highly labeled KNO_3 in 30-times O^{18} -depleted water showed that the isotopic exchange between KNO_3 and water under similar conditions is not detectable. The traces of KNO_2 formed in the electrolytic experiments using KNO_3 are mostly removed on crystallization and do not affect the analytical result. Attempts to separate the nitrate from the organic solvent by thin layer chromatography were not successful.

For mass spectrometric analysis at least 5 mg of any compound is required for a single isotopic analysis. Quantities smaller than this give irreproducible results, due in part to exchange with traces of moisture, impurities, etc., in the glassware.

Mass spectrometric analysis.—Water was analyzed by mass spectrometry using conventional methods. At low enrichments the "bromine" method was used by means of which water is converted to molecular oxygen by alkaline hypobromite (11). At high enrichments the water is equilibrated with carbon dioxide (12); at very high enrichments O^{18} -labeled CO_2 is used to avoid too great an isotopic dilution. The oxygen or carbon dioxide was analyzed by mass spectrometry. Attempts to equilibrate CO_2 directly with water mixed with either NMA or glycol were not successful.

Potassium nitrate was analyzed by two methods: a general method for pyrolysis of inorganic materials to carbon dioxide by means of a mixture of mercuric chloride and mercuric cyanide (13) and a specific method for nitrate in which the oxygen is converted to nitrous oxide by pyrolysis with ammonium chloride (14). Both methods gave the same result.

Glycol and NMA were analyzed for their isotopic content by conversion to carbon dioxide by the pyrolytic method described above. However, in order to obtain reproducible results great care must be taken to purify the carbon dioxide before mass spectrometric analysis. The gas was first passed through a column of benzoquinoline crystals in order to absorb HCl and

other acidic substances and then distilled from -80°C (dry ice acetone) to a liquid nitrogen trap. CO_2 purified in this manner gave reproducible results.

Attempts to analyze the oxygen isotopic content of NMA and glycol nondestructively by means of infrared (O^{18}) or NMR (O^{17}) were not successful owing to the low sensitivity of these methods.

Isotopic analysis of the anodic oxide films.— O^{16} was measured by the O^{16} (d,p) O^{17*} reaction and O^{18} by the O^{18} (p, α) N^{15} reaction. The technical details of these nuclear methods, devised for the study of anodic oxidation processes, are described in ref. (4) and (5). Other applications to anodic oxidation were described in ref. (6) and (7).

Results

Chemical Changes in the Electrolytes

The effects on the electrolyte of the electrochemical processes taking place during anodic treatment depend on the nature of the currents injected into the electrodes. At the cathode, by choosing a platinum electrode, we insured that this current is purely electronic. At the anode both electronic and ionic currents may pass through the oxide layer being formed. In what follows we shall discuss the various effects of the anodic current in terms of "electronic" and "ionic," it being understood that this refers to its nature in the oxide layer.

Since the current efficiency of the anodic oxidation of silicon is of the order of only 2%, it would appear that most of the current is used up in decomposing the solution, as is illustrated by the poisoning effects mentioned above. Some of the products of anodic processes have been studied by Duffek *et al.* (2, 3), who showed that the amount of silicon lost to the electrolyte is a small fraction of that contained in the oxide film formed. They also found that water was formed during the electrolysis. We have investigated some of these phenomena including the formation of water, both by effective drying of the solvents before use and also by using O^{18} as a tracer.

Measurements in a single-compartment cell.—In order to simulate the electronic current, corresponding to the small current efficiency of silicon oxidation, a given quantity of electricity was passed between platinum electrodes in the above solutions. The cell used is shown in Fig. 2. The formation of water was studied as a function of the components of the solution and of the current passed. A new solution was used for each measurement, so that each experiment is influenced in the same way by traces of water accidentally introduced. The total amount of water thus introduced into a 20 ml solution from outside sources (*i.e.*, before electrolysis) is estimated to be about 5 mg.

Figure 3 shows the results for NMA and glycol solutions containing 0.4% KNO_3 . The presence of traces

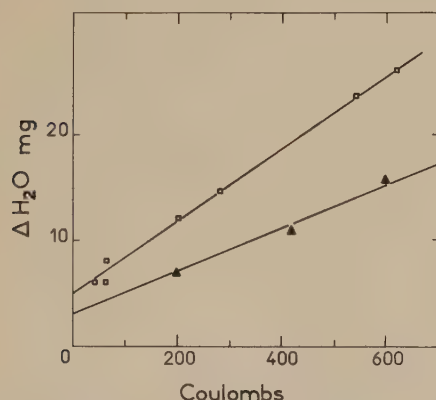


Fig. 3. Formation of water during electrolysis in a single compartment cell, as measured by Karl Fischer method: $\square$ glycol, $\blacktriangle$ NMA.

Table I. Water formation in a single compartment cell

H_2O formed	Glycol	NMA
mg/1000 coulomb	40	20
mole/Faraday	0.2	0.1

of water from outside sources is shown by extrapolating the straight lines to the origin. The proportionality constant between the net increase in the amount of water and the charge passed can be deduced from these results for various solutions (Table I). The results for glycol and KNO_2 system are very similar to those for KNO_3 . Thus, these two salts appear to be equivalent from this point of view.

These experiments were repeated in glycol solutions with a silicon anode, with results identical to those obtained above with platinum. This confirms that the effects in the oxidation process of silicon were indeed due to an electronic current.

Measurements in a three-compartment cell.—In order to investigate the formation of water in more detail, measurements were carried out in a three-compartment cell, using either NMA or glycol solutions containing 0.4% KNO_3 and platinum electrodes. Only hydrogen was evolved at the cathode as verified by mass spectrometry, the yield obtained by coulometric measurements being exactly 1 g-atom/Faraday. Although under normal circumstances no gas evolution was observed at the anode, precise coulometric experiments at high current densities performed with a special cell indicate that small amounts of gas may be evolved.

In NMA, after the passage of 1000 coulombs, an increase in the pH at the cathode was observed, which has been attributed to the formation of KOH [see ref. (2)]. Simultaneously, the pH at the anode fell to about 5. Further results are given in Table II.

The reduction of nitrate to nitrite is negligible as the total amount of nitrite formed corresponds to the consumption of only 0.3 coulombs, 3×10^{-4} of the quantity passed. The presence of nitrite in the anode and middle compartments can be attributed to a migration process from the cathode. Similar results were obtained in glycol. Duffek *et al.* (2, 3) also found traces of nitrite after anodic oxidation but did not estimate the extent of this process.

The amount of the water formed varies from compartment to compartment. The increase in the water content of the middle compartment could be due to transport phenomena by electrolytic migration or spontaneous diffusion from the anode compartment. Experiments have shown that the quantity of water is independent of the porosity of the sintered glass partitions for porosities of between 1 and 4 (*i.e.*, 120–10 μ) indicating that migration is probably preponderant. The total amount of water formed in all three compartments is significantly greater than that found in a single-compartment cell under similar conditions for both NMA and glycol solutions. As will be discussed later, this suggests that water is probably formed at the anode and destroyed at the cathode. This suggestion is supported using O^{18} tracers and nuclear analysis of the oxide films (see below). Direct methods such

Table II. Decomposition products in a three-compartment cell

	Anode	Middle	Cathode	Total
(a) NMA				
KNO_3 formed:				
mg/1000 coulomb	2.5×10^{-2}	2.5×10^{-2}	8.5×10^{-2}	1.3×10^{-1}
mole/Faraday	3×10^{-5}	3×10^{-5}	10^{-4}	1.6×10^{-4}
H_2O formed:				
mg/1000 coulomb	50 to 60	15 to 20	Negligible	65 to 80
mole/Faraday	~ 0.3	~ 0.1		~ 0.4
(b) Glycol				
H_2O formed:				
mg/1000 coulomb	70 to 100	10 to 40	0 to 20	120 to 140
mole/Faraday	0.4 to 0.5	0.1 to 0.2	0 to 0.1	~ 0.7

as these eliminate the uncertainties due to transport phenomena.

Isotopic Changes in the Electrolytes

Since all the components of the solutions contain oxygen, tracer experiments by O^{18} labeling of one of the constituents can only be simply interpreted if the changes in the isotopic compositions throughout the experiment are relatively slow. Therefore the isotopic oxygen exchange between the components of the solution was studied in detail first by mass spectrometry and these results will be presented now. They will be followed by those on the labeling of the films obtained by oxidation.

Temperature induced exchange.—Solutions of NMA and glycol containing either water or nitrate labeled with O^{18} were heated to 100°C or more for times of up to 720 hr. The isotopic composition of each constituent was analyzed in a mass spectrometer before and after heating. The absolute errors on the results are taken as $\pm 0.02\%$ for concentrations at or near the natural abundance of O^{18} and $\pm 0.5\%$ for higher concentrations. The results obtained are given in Table III, where the calculated exchange ratios of the various constituents are shown. These ratios were calculated for the exchange between two constituents as follows. Since the kinetics of the isotopic exchange obey a first order kinetic law (15), the exchange ratio, ρ , after a heating time t , may be written as

$$\rho = \frac{C(o) - C(t)}{C(o) - C(\infty)} = 1 - e^{-t/\tau}$$

where $C(o)$ is the initial concentration of isotope in the constituent examined, $C(\infty)$ the concentration of isotope at equilibrium for a total exchange, and τ the mean life, characteristic of the exchange. In the three component systems (NMA + H_2O + KNO_3) the calculations were made separately for the pairs NMA + H_2O , KNO_3 + H_2O , neglecting the effect of the third component, since the extent of the exchange is small. The results indicate that in all cases studied, the exchange ratios are less than 2%. Those calculated for each constituent in glycol are in good agreement with one another, but in the case of NMA the water could not be analyzed. The mean life τ deduced from ρ is shown in Table IV.

From these results the following conclusions may be drawn:

Exchange in NMA.—The results indicate that there is a very slow isotopic exchange of oxygen between NMA and water at 100°C . Both with and without added KNO_3 the exchange ratio is of the order of 0.5%, corresponding to a mean life of 1.5×10^5 hr; a mechanism

for isotopic exchange of oxygen between amides and water in dilute solution is known [see ref. (16)] and may operate here. The exchange at 100°C between KNO_3 and water dissolved in NMA occurs at a slightly higher rate. This exchange is known to occur but is acid catalyzed; under the drastic conditions of the experiment, the presence of traces of acid (from hydrolysis of NMA for instance) cannot be excluded. Under the considerably milder conditions used for anodic oxidation, (i.e., a few hours at room temperature) thermal exchange of oxygen between the various components in the NMA system can be ruled out.

Exchange in glycol.—The isotopic exchange of oxygen between water and glycol is somewhat faster than with NMA as shown by the isotopic analysis of each component after 148 hr at 100°C . Various dehydration, hydration, and substitution mechanisms for this exchange can be postulated, but at the present time there is insufficient evidence for deciding which mechanism operates. There is virtually no exchange between glycol and nitrate, as might be expected. Here again the thermal isotopic exchange of oxygen is so slow as not to be taken into account under the considerably milder conditions of anodic oxidation.

Electrochemically induced exchange.—The isotopic labeling of a component in an electrolyte mixture under the influence of an electric current passing through the cell, could be the result of various processes:

1. the formation by electrolytic decomposition of products which can exchange oxygen rapidly with the other components of the solution;
2. the formation of nonlabeled species, chemically identical to the labeled ones; causing isotopic dilution;
3. exchange induced by the electrolysis itself.

The experiments carried out were on NMA solutions where isotopic analysis of all the components was possible, and on glycol solutions where only the glycol could be analyzed. The results obtained in the three-compartment cell may also be affected by transport phenomena; their effect on the accuracy of the results for water is smaller here than in the experiments on thermal exchange in the electrolyte, since larger quantities of labeled water are used.

The NMA- KNO_3 - H_2O system.—The results of the mass spectrometric analysis are summarized in Table V. They show that:

1. there is no change in the isotopic content of the water from the middle and cathode compartments, within experimental error;
2. the isotopic content of oxygen in the water in the anode compartment decreases markedly;
3. the isotopic content of oxygen in the NMA hardly changes;

Table III. Temperature induced exchange

Bath	Exchange conditions	Oxygen content, mole	Original labeling, $C_o = \frac{O^{18}}{O^{16} + O^{18}} \%$	Equilibrium labeling, $C_e, \%$	Final labeling, $C_t, \%$	Exchange ratio, $\rho, \%$
NMA 5g	720 hr, 100°C	7×10^{-2}	0.2	12.4	0.28	0.65
H_2O 0.5g		2.5×10^{-2}	47	—	—	—
NMA 5g	720 hr, 100°C	7×10^{-2}	0.2	12.4*	0.28	0.65*
H_2O 0.5g		2.5×10^{-2}	47	—	—	—
KNO_3 0.05g		1.5×10^{-3}	0.2	45**	1.06	1.9**
Glycol 4g	148 hr, 100°C	1.3×10^{-1}	0.2	13.1	0.45	1.9
H_2O^{18} 0.5g		2.5×10^{-2}	81.2	13.1	80.1	1.6
Glycol 4g	148 hr, 197°C	1.3×10^{-1}	0.2	2.3	0.2	Negligible
KNO_3 0.15g		4.3×10^{-3}	59.5	2.3	59.4	Negligible

* Calculated for the couple NMA- H_2O .

** Calculated for the couple H_2O - KNO_3 .

Table IV. Exchange mean life

Couple	NMA/ H_2O	Glycol/ H_2O	Glycol/ KNO_3	H_2O / KNO_3
Exchange conditions				
Time (hr)	720	148	148	720
Temperature ($^\circ\text{C}$)	100	100	197	100
Mean life (hr)	1.5×10^5	1.6×10^4	Too large to measure	8×10^4

4. the isotopic content of oxygen in the nitrate is unchanged (this analysis was made on KNO_3 from a solution where 500 coulombs have been passed to oxidize silicon samples). These results are compatible with those obtained in the preceding section.

In the anode compartment the change in the isotopic content of oxygen in the water does not correlate quantitatively to the change in the opposite direction of isotopic content of the NMA and nitrate. This is not, therefore, the result of exchange phenomena, but of isotopic dilution, in agreement with the production of water indicated earlier. The decrease in O^{18} content of the water in the anode compartment from 68 to 60% can be accounted for by the creation of 5×10^{-3} moles of water per 100 coulombs, i.e., about 0.5 mole/Faraday. This last figure is in agreement with that obtained by the classical methods previously described. The interpretation of this result will be discussed later.

The glycol- KNO_3 - H_2O systems.—Similar experiments in glycol have lead to the results given in Table V. The isotopic analysis of oxygen in glycol shows that there is again a slight change, varying from one compartment to the other.

It appears that apart from the dilution effect due to the formation of water at the anode there is little isotopic exchange between the constituents of both NMA and glycol solutions even after 1000 coulombs have been passed through the solution. Since less than 200 coulombs are required for the formation of an anodic oxide film on silicon, electrochemically induced isotopic exchanges can be neglected.

The formation of water and consequent changes in isotopic oxygen content can be examined by analyzing the oxide layers formed. Once it has been established that the isotopic exchanges between the components of the solutions are very slow, and can be neglected, one can determine the source of oxygen and the production of water with greater accuracy and care by the nuclear methods outlined above.

Isotopic Analysis of the Oxide Films

The oxygen necessary for the formation of tantalum and silicon oxides can be provided by any of the components of the solution. It is unlikely that the source of oxygen is dissolved molecular oxygen (see Discussion). The relative contribution of oxygen from each of the constituents of the solution to the oxide layer was evaluated by using labeled H_2O^{18} and KNO_3^{18} , which have been shown not to undergo isotopic exchange under a wide variety of conditions.

Both tantalum and silicon were oxidized. Because of the high yield in the anodic oxidation of tantalum and consequent minimal decomposition of the solution, tantalum oxides were considered to be characteristic of the isotopic composition of the solution at various stages. In order to verify that current density does not affect the process investigated, some experiments were made at 5 mA/cm² on silicon, in addition to all those made at 1 mA/cm². No difference was observed between them.

Table V. Electrochemically induced exchange

Bath		% O^{18} initial	Charge passed through, coulombs	% O^{18} final		
				Anode	Middle	Cathode
NMA	30g	0.2	1000	0.32	0.33	0.44
H_2O^{18}	2g	87		82.5	85.9	86.3
NMA	30g	0.2		0.210	0.215	0.270
H_2O^{18}	2g	68	1000	60	68	67.5
KNO_3	100 mg	0.2	500	—	—	—
NMA	30g	0.2		—	—	—
H_2O^{18}	100 mg	0.2		—	—	—
KNO_3^{18}	100 mg	77	1000	75.5*	75.5*	75.5*
Glycol	25g	0.2		0.204	0.204	0.230
H_2O^{18}	2g	72		—	—	—
Glycol	25g	0.2	1000	0.215	0.207	0.500
H_2O^{18}	2g	72		—	—	—
KNO_3	100 mg	0.2		—	—	—

* Single compartment cell, silicon anode.

In what follows the isotopic O^{18} content, i.e., the $\text{O}^{18}/(\text{O}^{16} + \text{O}^{18})$ ratio, of the oxides will be called C . In the calculations the O^{17} content, always less than 0.5%, was neglected. The quantity of interest is often the isotopic oxygen content normalized to 100% enrichment of the labeled species. This quantity will be written C^* .

O^{18} -labeled water.—It should be emphasized that during anodic oxidation it is the total amount of water produced which contributes to the isotopic dilution, since stirring mixes water from various origins completely before destruction at the cathode. In order to minimize the errors caused by dilution, the oxide layer formed in a fresh solution at the beginning of a series of oxidations (immediately after the Karl Fischer analysis) was analyzed for its O^{18} content. From this result the proportion of oxygen originating from the water can be calculated. Then, by following the isotopic content of subsequent oxide layers on a series of anodes, in the same solution, the dilution effect was measured and the rate of creation of water determined.

Experiments were carried out in the following solutions



The water added to the "dry solvent" had a concentration of 88% O^{18} , but the introduction of traces of water during handling operations (as determined by the Karl Fischer method) reduced the actual isotopic concentration of the water in the solution at the start of the oxidations to $76 \pm 2\%$ O^{18} . In both NMA and glycol and for both silicon and tantalum oxidations, the isotopic content C of the first oxides produced in repeated experiments on fresh solutions was $67 \pm 1\%$. The SiO_2 films were formed at 150V (consuming 40 coulombs) and the Ta_2O_5 films at 50V (with a consumption of less than 0.5 coulomb). A tantalum foil was oxidized before and after each silicon oxidation. Dilution of the O^{18} content due to the 40 coulombs used for the first silicon oxidation was less than 2%. When O^{18} -washed solvents (see above) were used, identical results were obtained, confirming the efficiency of our drying and analytical techniques. Calculation of the normalized isotopic content C^* shows that $88 \pm 3\%$ of the oxygen in the oxides (both silicon and tantalum in NMA or glycol) comes from the water in these conditions.

The isotopic oxygen content of a series of films formed in successive oxidations in the same bath was examined. The solutions used were similar to those described in preceding experiments. Ta and Si samples were alternately oxidized in NMA solutions, the cell being opened only after three pairs of oxidations. For glycol solutions the procedure was somewhat different. Si and Ta were oxidized in separate solutions. Between each oxidation of Ta, the effect of the oxidation of Si was simulated by letting a current flow between Pt electrodes so as to consume 180 coulombs. This checked the equivalence of the electrolytic effect due to the passage of electronic current with silicon or platinum anodes.

Results are shown in Fig. 4 and 5. It was found convenient to plot in these figures the quantity $\Delta(W_0^{18}/C)$ (where W_0^{18} is the total amount of O^{18} -labeled water molecules present initially in the fresh solution) as a function of the number of coulombs passed through the cell. The theoretical basis for the choice of this plot is discussed below. It should be noted however that were the water the only source of oxygen and were there no destruction of water, one would have

$$C = \frac{W_0^{18}}{W_0^{18} + W^{16}}$$

where W^{16} is the amount of unlabeled water in the solution at any instant. Then

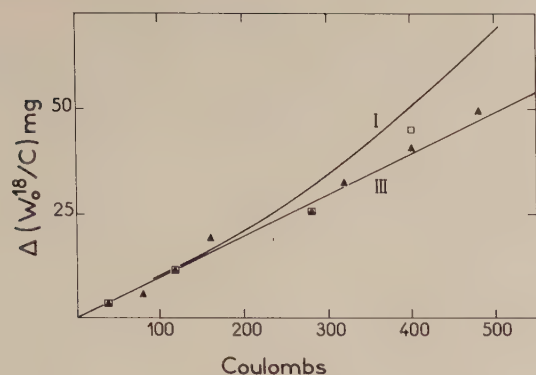


Fig. 4. Change in the isotopic content C of the oxide layer during oxidation in an NMA bath containing O^{18} labeled water. $\square$ Silicon, $\blacktriangle$ tantalum. The calculated curves correspond respectively to cases I and III.

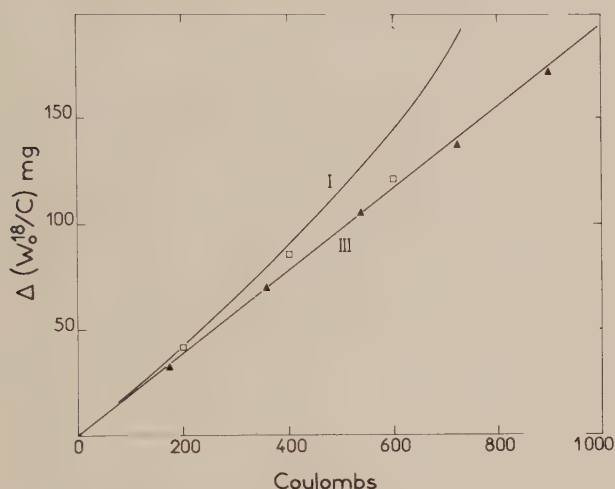


Fig. 5. Change in the isotopic content C of the oxide layer during oxidation in a glycol bath containing O^{18} labeled water. $\square$ Silicon, $\blacktriangle$ tantalum. The calculated curves correspond respectively to cases I and III.

$$\Delta \left(\frac{W_o^{18}}{C} \right) = \Delta W^{16} \quad [1]$$

and the water production could be simply deduced from Fig. 4 and 5 by measuring the slope. A more sophisticated interpretation of the results would require experiments using O^{18} -labeled KNO_3 .

It is seen from Fig. 4 and 5 that the results for both silicon and tantalum oxide films fall approximately on a single line, suggesting that the source of oxygen is the same for the oxidation of both anodes.

O^{18} -labeled KNO_3 .—Solutions of KNO_3^{18} (enriched to 77% O^{18}) in either NMA or glycol and water (all of natural isotopic composition) were used to further investigate the sources of oxygen for the oxidation of silicon and tantalum.

Alternate oxidations of Si and Ta were carried out in the same NMA solution by the procedure previously described. The highest normalized O^{18} -content C^* of the films obtained (both Si and Ta) in a freshly prepared 0.4% KNO_3^{18} + 0.4% H_2O + NMA solution was $10.6 \pm 1\%$. This value is discussed below. After a series of Ta-Si pairs of oxidations in the same solution where the change in isotopic content was very slow, successive injections of unlabeled water were added to the solution between each Ta-Si pair in order to elucidate the effect of salt to water ratio. Each injection added an increment of 0.2% of water to the system. The results are shown in Fig. 6 where the inverse of the normalized isotopic content C^* of the oxides is shown as a function of the quantity of water

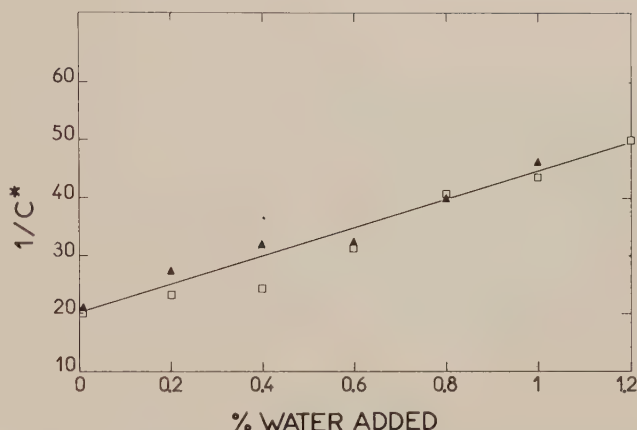


Fig. 6. Dependence of the normalized content C^* of the anodic oxides on the amount of water added to NMA solutions containing O^{18} labeled KNO_3 . $\square$ Silicon, $\blacktriangle$ tantalum.

added (the effect of electrochemically produced water being neglected). It is seen again that the isotopic content of the silicon and tantalum oxides is very similar. The straight line obtained indicates that the relationship between O^{18} content and water added is homographic.

Similar results were obtained for SiO_2 films produced in glycol indicating that the nature of the solvent does not play a critical role in the function of the salt as a source of oxygen. On the other hand, Ta_2O_5 films produced in glycol contained slightly more O^{18} than SiO_2 films. This discrepancy may be due to the difficulties in oxidizing tantalum in glycol containing KNO_3 which produces films of bad quality and ill-defined composition, even when formed at voltages near 20V.

Incorporation of nitrate in the anodic oxide films.—One obvious reason for the presence of O^{18} in anodic oxides from labeled KNO_3 could be the direct incorporation of NO_3^- or NO_2^- anions into the film [as discussed in a similar case in ref. (7)]. It was therefore important to determine the nitrogen content of oxide films formed in NMA and glycol solutions containing 0.4% KNO_3 and 0.4% water. Nitrogen was measured using nuclear reaction microanalysis, by means of the $N^{14}(d,\alpha)C^{12}$ reaction as described in ref. (17). This sensitive analytical technique allowed us to assign an upper limit to the nitrogen content of the films. This limit was set by the presence of traces of nitrogen on the samples before anodic oxidation. The SiO_2 films formed in both glycol and NMA solutions were found to contain less than 0.2% nitrogen, per oxygen atom. The tantalum oxide films formed in NMA contained less than 0.8% nitrogen per oxygen atom. However, those formed in glycol containing KNO_3 contained a significant amount of nitrogen up to 2.5%, but as stated above, these films are of poor quality and results are probably not reliable.

It thus appears that direct incorporation of nitrogen containing anions accounts for less than 0.6% of the oxygen in SiO_2 and less than 2.4% in Ta_2O_5 . In order to account for the 11% oxygen originating from nitrate found, a more complex mechanism of oxygen transfer from salt to oxide must be considered.

Quantitative Interpretation of Results

Empirical relationships for the sources of oxygen.—Let α , β , and γ be the relative contributions to the source of oxygen of the salt, the water, and of the solvent, respectively. We have

$$\alpha + \beta + \gamma = 1 \quad [2]$$

For equal weights of salt and water it was found experimentally that in all cases

$$\alpha = 10.6 \pm 1\% \quad \text{and} \quad \beta = 88 \pm 3\%$$

hence

$$\alpha + \beta = 98.6 \pm 3\%$$

This shows that γ is negligible, i.e., that within the experimental error the oxygen of the solvent does not constitute a direct source of oxygen.

The laws governing the contributions α and β as a function of salt and water concentrations in the solutions may be deduced from Fig. 6, using certain simple assumptions. Let V_o be the quantity of solvent used in the labeled KNO_3 experiment, S and W the amounts of salt and water (expressed in moles) at various stages. The isotopic O^{18} content of the oxide films is

$$C = \alpha\eta$$

where η is the isotopic content of the oxygen of the salt (77% in this case). We have shown that η is constant throughout the experiment. Whereas S is constant, $S = S_o$, W varies as water is added to the solution. Hence

$$\alpha = f(W, S_o)$$

where S_o is a fixed parameter. From Fig. 6 one can deduce, since here $C^* = \alpha$ that

$$\frac{1}{f(W, S_o)} = KW + l$$

K and l being constants.

This formula may be written in the form

$$\frac{1}{f(W, S_o)} = k \frac{W}{S_o} + l \quad [3]$$

where k and l are now dimensionless constants.

The value of k may be obtained from Fig. 6: $k = 1.8 \pm 0.2$. Using this value and the value $10.6 \pm 1\%$ for C^* for equal weights of salt and water, one may obtain the value of l , which is not far from unity. However, this value is not well defined since it is deduced by extrapolation over a wide interval. If we assume $l = 1$, one may write

$$\alpha = f(W, S_o) = \frac{S_o}{kW + S_o} \quad [4a]$$

and since $\alpha + \beta = 1$

$$\beta = \frac{W}{k^{-1}S_o + W} \quad [4b]$$

Thus, assuming $l = 1$, the amount of salt S_o is equivalent to an amount $W_e = k^{-1}S_o$ of water. A slightly different value of l would give a more complex homographic relation for α and β , without changing the numerical values appreciably.

The above calculation was based on the hypothesis that $S = S_o$, and in principle k (like l) depends on S . If the simple equivalence law found above applies in a limited range of values of S and W (for given V_o), it is most probable that k is independent of S . This implies, in fact, the assumption that the source of oxygen depends only on the ratio W/S of the water to salt concentrations, and not on the absolute concentrations with respect to the solvent. Whereas no detailed experimental proof of the general validity of Eq. [4a] and [4b] can be given, some measurements made with 0.2% of salt by weight of solvent have confirmed the validity of these laws within the range of experimental conditions studied. Further discussion of this result is given below.

Equations [4a] and [4b] may be tested for the values of α and β measured for equal weights of salt and water with $k = 1.8 \pm 0.2$ and, assuming that $l = 1$. One finds that

$$\alpha = 9 \pm 1\% \quad \text{and} \quad \beta = 91 \pm 3\%$$

which compare well with the values $\alpha = 10.6 \pm 1\%$ and $\beta = 88 \pm 3\%$, found experimentally by independent experiments.

The production and destruction of water.—The experimental results on the production and destruction of electrolytic water (measured using O^{18} -labeled water), shown in Fig. 4 and 5, cannot be interpreted by means of the simple formula [1], since the following facts must be taken into account.

(i) A quantity of $q\theta$ of water is produced by θ coulombs (the number of coulombs passed through the cell), with isotopic composition identical to that of the solvent, i.e., natural abundance.

(ii) A quantity $\hat{q}\theta$ of water is destroyed by θ coulombs; the isotopic composition of the water destroyed is the same as that of all the water in the solution, assuming isotopic homogeneity due to good stirring.

(iii) The O^{18} contained in the destroyed water molecules remains in the solution since the oxygen evolved as a gas at the cathode and the anode is negligible.

(iv) The source of oxygen is the water and the salt according to Eq. [4a] and [4b]. The water equivalent $W_e = k^{-1}S_o$ does not participate in the production or destruction phenomena and is of natural isotopic composition throughout (the salt is not labeled in this experiment).

It appears at this stage that in order to interpret the experimental results an additional assumption on the role of the O^{18} atoms which are removed from water is needed. Water is here considered to be all species detected by the Karl Fischer method in the solution. Three simple cases may be considered:

Case I. The new compounds which contain O^{18} do not oxidize the anode and do not undergo isotopic exchange with water. Hence, the corresponding O^{18} atoms do not play a role in further anodic processes.

Case II. The new compounds behave like water for anodic oxidation but are not detected by Karl Fischer titrations. In this case the amount of O^{18} atoms to be considered remains constant.

Case III. The new compounds do not act as a direct source of oxygen but are in isotopic equilibrium with the water in the solution.

The real situation may be a mixture of these various possibilities. In order to interpret our results we have calculated the theoretical curves corresponding to those three models, the calculation being given in the Appendix. The curves corresponding to case I and case III were drawn for NMA in Fig. 4, and for glycol in Fig. 5.

It thus appears that case I is not supported by the experimental results, whereas case III is in excellent agreement with the experimental points for both Ta and Si. Case II gives rise to two possibilities:

Case IIa. That the quantity W in formula [4a] and [4b] represents the total amount of oxygen-supplying compounds. In this case it appears as if there is no water destruction at all and that the phenomenon obeys Eq. [1].

Case IIb. The quantity W in Eq. [4a] and [4b] is the water detected by the Karl Fischer method. Then as shown in the Appendix, the calculated curve is identical with that of case III. These assumptions are discussed below.

It should be noted that case III leads, in the range of values studied, to a nearly linear relation, and the only difference between case III and case IIa is in the calculated value of the rate of water production.

The following rates of water production (q) are thus obtained:

Case III: 9.05 g/F in NMA; 17.9 g/F in glycol.

Case IIa: 9.85 g/F in NMA; 19.3 g/F in glycol.

Discussion

The results may be best discussed in relation to two well-defined classes of phenomena: changes induced in the electrolyte by electronic current and the anodic oxidation processes induced by ionic current.

Action of the electronic current on the electrolyte.—First, a choice should be made between case IIa and

case III which give slightly different values for the rate of water production. Case IIb, which gives the same results as case III, seems less likely as, if the decomposition products behave like water for oxygen supply they should also behave like water with respect to the salt. We have no experimental evidence to decide between cases IIa and III. However, it seems less likely that a compound behaves exactly like water for oxygen supply in anodic oxidation and not in titration by the Karl Fischer method. On the other hand, experiments have shown that in the organic solutions used, KOH is detected as water by the Karl Fischer method within experimental error, in agreement with ref. (18) (1.251). As a result the concentration of KOH is included in the amount of water formed when describing our phenomena. Under these conditions (with a 10% error if case IIa is the correct one), our results may be summed up with the statement that approximately 0.5 mole of water per Faraday is created in NMA by the electronic current and 1 mole/Faraday in glycol.

Any mechanism for this process must therefore account for the following facts:

(a) about 0.5 mole/Faraday of water is created at the anode in NMA, and 1 mole/Faraday in glycol; in both cases about 80% of the water produced is destroyed at the cathode.

(b) H^+ is produced at the anode and OH^- at the cathode.

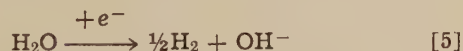
(c) Hydrogen is evolved at the cathode. Negligible gas evolution is observed at the anode during anodic oxidation of Si and Ta.

(d) Slight decomposition of the nitrate into nitrite was measured.

(e) Isotopic exchange of oxygen between nitrate, water, and solvents is negligible. However, a very small isotopic exchange between water and the solvents was observed, mainly at the cathode.

The reactions occurring can be discussed in terms of those related to the cathode and those to the anode.

Reactions at the cathode.—The primary reaction at the cathode is probably

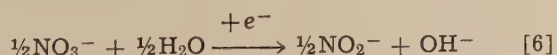


Some of the hydroxide ions formed attack the organic solvent causing it to hydrolyze. While no direct evidence for hydrolysis products could be obtained, the rapid poisoning of the system quoted above may indicate the liberation of such species.

There is some evidence for nucleophilic attack of hydroxide on NMA from the slight exchange of O^{18} observed, by the mechanism involving reversible addition of OH^- to the carbonyl bond as suggested by Bender and Ginger (19). In glycol solutions there is no evidence as to the nature of the exchange reactions.

In the presence of an electric current there is the possibility of the formation of aldehydic species: acetaldehyde in the case of NMA and either acetaldehyde, formaldehyde, or a related compound in glycol. The formation of such species would account for the existence of a compound with one oxygen which rapidly undergoes isotopic exchange with the water in the solvent [ref. (8), p. 55; and ref. (20)]. Carbonyl compounds are not easily analyzed by Karl Fischer titrations and in fact formaldehyde is unaffected by the analytical reagent [ref. (18), p. 147]. Although no positive evidence for an aldehydic species has been obtained, the presence of these entities would account for most of the experimental observations.

The reduction of nitrate to nitrite at the cathode takes place according to the reaction



The quantitative measurements of nitrite showed however that this reaction accounts for such a small por-

portion of the current (3×10^{-4}) that its effect as a pathway for the loss of water is negligible.

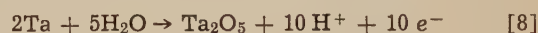
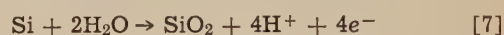
Reactions at the anode.—The main reaction at the anode which must be considered is the production of water. It can be assumed that the oxygen of this water comes from the organic solvents in each case, since the only other source, nitrate, can be eliminated from the O^{18} -labeling experiments. Various condensation reactions of organic compounds (both amides and alcohols) can be suggested to account for water production (21). However, in the absence of isolatable products, no mechanism for the production of water can be suggested at the present time. It should be noted that the yield of water in glycol where there are two oxygen atoms is exactly double that in NMA where there is only one. This may be related to the mechanism, but the possibilities of a coincidence cannot be excluded. The most important reaction at the anode is of course the anodic oxidation of silicon and tantalum.

Anodic oxidation processes.—The phenomena investigated may be described as follows:

(a) Although their oxidation current efficiencies are very different, in all these experiments silicon and tantalum behaved in an identical manner. It therefore seems very likely that the reactions induced by the electronic current do not affect the mechanism for the supply of oxygen for anodic oxidation. Since in silicon oxidation water is produced, the similarity to tantalum indicates that this water must be immediately mixed with the bulk of the solution, so as to insure isotopic equilibrium.

(b) The source of oxygen in anodic oxidation does not depend on the nature (NMA or glycol) of the solution.

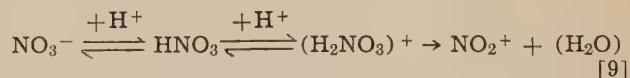
(c) The organic molecules do not act as a direct source of oxygen in anodic oxidation. The contribution of the two identified oxygen sources, water and nitrate, depend on their relative concentrations according to Eq. [3] and [4a] and, at least at low absolute concentrations, not on the nature of the solvent. The over-all equations for the reaction with water, which is the main source of oxygen, may be written as



(d) The nitrate is also a supplier of oxygen as a direct source, since no incorporation of nitrogen or isotopic exchange with water was observed.

External molecular oxygen can play no role in the reaction since all solutions were carefully degassed before use. As was mentioned above, in cells of special geometry, some molecular oxygen may be evolved at the anode during oxidation. This however is not likely to be a source of oxygen by means of electrochemical reactions at the anode.

A tentative mechanism for the direct participation of nitrate in anodic oxidation is the following. The protons formed by the reaction [7] and [8] (and in the case of silicon, also those formed by the electronic current) could react with nitrate ions near the surface of the anode. The reaction will loosen the oxygen to nitrogen bonds possibly through a nitronium type of reaction (22), thereby providing another source of oxygen for oxide formation, the reaction being of the following type



the water species immediately reacting with the anode to form an oxide. The high local concentration of protons near the anode is such that a fixed fraction of the nitrate ions undergoes this process, independently of absolute water concentration and current density. This dependence on local protonation makes these reactions

very sensitive to possible acidity of the salt and to the environment. The two competing sources of oxygen contribute in proportion to the relative concentration of water and salt (assuming that the concentrations are the same near the anode as in the bulk of the solution). The weighting factor k of Eq. [4a] is determined by the fraction of the nitrate ions which undergoes reaction [9]. Whatever the mechanism is, the fact that k is the same for silicon and tantalum is not surprising considering their similar electrochemical properties, the oxidation reduction potentials, for reactions [7] and [8] being 0.86 and 0.81V, respectively, on the hydrogen scale.

APPENDIX

One may calculate the O^{18} content $C(\theta)$ of the oxide films as a function of the charge θ passed through the cell using Eq. [4a] and [4b] and the assumptions corresponding to cases I, II, and III. The calculations enable one to extract from Fig. 3, 4, and 5 the value of the rate of production and destruction of water, knowing the initial total water content (in moles) W_o of the solution, and the initial number of moles, W_o^{18} of the O^{18} -labeled water molecules. The total water content is for any θ

$$W(\theta) = W_o + (q - \hat{q})\theta \quad [A-1]$$

This relation was used to extract the values of $(q - \hat{q})$ from Fig. 3, listed in Table I, which were used in the calculations below.

In all cases one may write for any θ , neglecting the O^{17} content

$$W(\theta) = W^{16}(\theta) + W^{18}(\theta) \quad [A-2a]$$

Moreover, the new decomposition products formed contain a number of moles U of oxygen where

$$U = \hat{q}\theta \quad [A-2b]$$

We may write

$$U(\theta) = U^{16}(\theta) + U^{18}(\theta) \quad [A-2c]$$

and we have

$$U^{18} + W^{18} = W_o^{18} = \text{constant} \quad [A-2d]$$

since the total number of O^{18} atoms is conserved.

Case I.—Here the only source of oxygen 18 is the water, and

$$C(\theta) = \beta(W) \frac{W^{18}(\theta)}{W(\theta)} \quad [A-3]$$

where $\beta(W)$ is the fraction of oxygen in the oxide originating from the water, for fixed salt content S_o and variable water content W . We may write from [4b]

$$\beta(W) = \frac{W}{W_e + W} \quad [A-4]$$

and

$$C(\theta) = \frac{W^{18}(\theta)}{W_e + W(\theta)} \quad [A-5]$$

The destruction of water may be described by the equation

$$\frac{dW^{18}(\theta)}{d\theta} = -\hat{q} \frac{W^{18}(\theta)}{W(\theta)} \quad [A-6]$$

according to assumption (ii) (Section on Production and destruction of water).

(a) If $\hat{q} = q$, $W(\theta) = W_o = \text{constant}$ and from [A-6]

$$W^{18}(\theta) = W_o^{18} \exp \left[-\frac{\hat{q}\theta}{W_o} \right] \quad [A-7]$$

(b) If $\hat{q} < q$, from [A-6] and [A-1]

$$\frac{dW^{18}(\theta)}{d\theta} \bigg/ W^{18}(\theta) = -\frac{\hat{q}}{W_o + (q - \hat{q})\theta}$$

Simple integration yields

$$W^{18}(\theta) = W_o^{18} \left[\frac{W_o}{W(\theta)} \right]^{q - \hat{q}} \quad [A-8a]$$

The closer $\hat{q}$ is to q , the closer $W^{18}(\theta)$ is approximated by an exponential.

$C(\theta)$ may be conveniently expressed from [A-5] and [A-8a] by writing

$$\frac{W_o^{18}}{C(\theta)} = \left[\frac{W(\theta)}{W_o} \right]^{q - \hat{q}} [W_e + W(\theta)] \quad [A-8b]$$

This expression was used to calculate the curves labeled I in Fig. 4 and 5.

The values of q and $\hat{q}$ to be used in [A-8b] are readily determined by noting that from [A-8b]

$$\frac{d \left[\frac{W_o^{18}}{C(\theta)} \right]}{d\theta} \bigg|_{\theta=0} = q + \hat{q} \frac{W_e}{W_o} \quad [A-9]$$

Hence the second term of Eq. [A-9] is determined by measuring the initial slope in Fig. 4 and 5. Knowing $q - \hat{q}$, q and $\hat{q}$ are calculated.

Case II.—Case IIa is described by Eq. [1] as mentioned above.

Case IIb is described by assuming that the new compounds formed behave for anodic oxidation like a quantity of water U , whereas β is still given by [A-4]. Hence,

$$C(\theta) = \beta \frac{W^{18} + U^{18}}{W + U}$$

Using [A-2d] we may write

$$\frac{W_o^{18}}{C(\theta)} = \left[1 + \frac{W_e}{W} \right] (W + U) \quad [A-10a]$$

and from [A-1] and [A-2b]

$$\frac{W_o^{18}}{C(\theta)} = \left[1 + \frac{W_e}{W} \right] (W_o + q\theta) \quad [A-10b]$$

It can readily be shown that the slope of this curve for $\theta = 0$ is also given by Eq. [A-9]. Hence both case I

and IIb lead to the same values of q and $\hat{q}$. On the other hand the expression [A-10b] is nearly linear in the range of values of θ considered here, as shown in Fig. 4 and 5.

Case III.—The isotopic equilibrium between the oxygen in the new compounds and the water in the solution, is expressed by

$$\frac{W^{18}}{W} = \frac{U^{18}}{U} = \frac{W_o^{18} - W^{18}}{U} \quad [A-11]$$

the last term being deduced using [A-2d]. Solving for W^{18} one gets

$$W^{18} = \frac{W_o^{18} W}{U + W} \quad [A-12]$$

and as [A-3] and [A-5] fully apply here also, according to assumption (ii) (Section on Production and destruction of water)

$$C(\theta) = \frac{W}{W_e + W} \frac{W_o^{18}}{U + W} \quad [A-13]$$

hence

$$\frac{W_o^{18}}{C(\theta)} = \left[1 + \frac{W_e}{W} \right] (W_o + q\theta)$$

which is identical with [A-10b]. Thus case III and IIb lead to the same result as stated above.

Acknowledgments

We wish to acknowledge the assistance of J. Diaz, P. Paimblant, and R. Venard of the SESCOSEM on

making many of the measurements reported here and of E. d'Artemare for his help in operating the Van der Graaff accelerator of E.N.S. In addition, we are grateful to Dr. J. Siejka for many enlightening discussions. The work was supported by CNRS (RCP No. 157), DGRST, and DRME.

Manuscript submitted June 19, 1970.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1971 JOURNAL.

REFERENCES

1. P. F. Schmidt and W. Michel, *This Journal*, **102**, 230 (1957).
2. E. F. Duffek, C. Mylroie, and E. A. Benjamini, *ibid.*, **111**, 1042 (1964).
3. E. F. Duffek, E. A. Benjamini, and C. Mylroie, *Electrochem. Technol.*, **3**, 75 (1965).
4. G. Amsel and D. Samuel, *J. Phys. Chem. Solids*, **23**, 1707 (1962); *Anal. Chem.*, **39**, 1689 (1967).
5. G. Amsel, C. Cherki, J. P. Nadai, and J. Siejka, Extended Abstracts, New York Meeting of the Society, May 4-9, 1969, p. 20.
6. G. Amsel and M. Croset, *ibid.*, p. 24.
7. G. Amsel, C. Cherki, G. Feuillade, and J. P. Nadai, *J. Phys. Chem. Solids*, **30**, 2117 (1969).
8. D. Samuel, "Methodology of Oxygen Isotopes," in "Oxygenases," O. Hayaishi, Editor, Interscience Publisher Inc., New York (1962).
9. M. Anbar, M. Halmann, and S. Pinchas, *J. Chem. Soc.*, **1960**, 1242.
10. M. Croset, *Rev. Sci. Instr.*, **37**, 123 (1966).
11. M. Anbar, *Intern. J. Appl. Radiation Isotopes*, **3**, 131 (1958).
12. M. Cohn and H. Urey, *J. Am. Chem. Soc.*, **60**, 659 (1938).
13. M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **4**, 233 (1959).
14. M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6243 (1955).
15. G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).
16. D. Samuel and B. L. Silver, "Advances in Physical Organic Chemistry," Vol. 3, p. 123, Academic Press, London (1965).
17. G. Amsel and D. David, *Rev. Phys. Appl.*, **4**, 383 (1969); and in "Proceedings of Grenoble Conference on MIS Structures," June 1969, p. 243.
18. J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers Inc., New York (1948).
19. M. L. Bender and R. D. Ginger, *J. Am. Chem. Soc.*, **77**, 348 (1955).
20. P. Greenzaid, Z. Luz, and D. Samuel, *Trans. Faraday Soc.*, **64**, 2781 (1968); and previous papers cited therein.
21. D. E. Couch, *Electrochim. Acta*, **9**, 327 (1964).
22. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," p. 276, G. Bell & Sons, Ltd. (1953).

ANNEXE

ANALYSE D'UNE COURBE D'EXCITATION AU VOISINAGE
D'UNE RESONANCE DE REACTION NUCLEAIRE.

MODELE STOCHASTIQUE POUR L'ETUDE DE LA PERTE
D'ENERGIE DES PARTICULES CHARGEES DANS LA MATIERE.

TABLE DES MATIERES

	<u>Pages</u>
I. <u>COURBE D'EXCITATION</u>	
A) Exposé du problème	1
B) Propriétés de $g(u,x)$	4
C) Propriétés de $N(E_0)$	5
1) Effet d'un absorbant	5
2) Cible homogène d'épaisseur infinie	6
3) Cible homogène d'épaisseur égale à X	7
II. <u>MODELE STOCHASTIQUE</u>	
A) Formule de Rutherford. Section efficace de collision	7
B) Modèle stochastique	9
1) Calcul des trois premiers moments centrés .	10
2) Cible homogène d'épaisseur infinie	14
3) Cible homogène d'épaisseur égale à X	16
4) Cible ayant un profil $C(x)$	17
5) Approximations pour le modèle stochastique	18
C) Méthodes de calcul de $g(u,x)$	20
1) Méthode directe	20
2) Méthode de Monte Carlo	20
3) Inversion de la transformée de Laplace	24
D) Approximations pour $g(u,x)$	28
1) Densité de probabilité gaussienne	28
2) Densité de probabilité	31
III. <u>COURBE D'EXCITATION THEORIQUE</u>	34
A) Résonance large	34
1) Applications à la résonance $O^{18}(p,\alpha)N^{15}$ à 629 KeV	36
2) Applications à la résonance $F^{19}(p,\alpha)O^{16}$ à 372 KeV	41
B) Résonance fine	41

I. COURBE D'EXCITATION

A) Exposé du problème

. La courbe d'excitation $N(E_0)$ représente le nombre total de toutes les particules provenant de la réaction nucléaire considérée en fonction de l'énergie E_0 du faisceau incident bombardant une cible de nature déterminée. On a la relation suivante :

$$N(E_0) = \left[\int_0^\infty dE \sigma_0(E) \left[\int_0^\infty C(x) g_0(E_0, E, x) dx \right] \right] \times \text{Constante} \quad (1)$$

où la constante (que nous égalons à l'unité par commodité) ne dépend que de l'angle solide et de l'efficacité de détection ainsi que du nombre de particules incidentes ; $\sigma_0(E)$ est la section efficace de la réaction nucléaire considérée à l'angle de détection θ pour l'énergie E d'une particule incidente. Il est utile de noter que pour des particules chargées la section efficace tend vers zéro avec E ; cet effet provient de la répulsion coulombienne exercée par le noyau. La fonction $C(x)$ représente le profil de concentration (exprimé en nombre de noyaux/cm³) des noyaux considérés dans la cible, au voisinage de la profondeur x . Nous négligerons, dans la suite, tout effet dû à l'agitation thermique des atomes de la cible.

. La fonction $g_0(E_0, E, x)$ est la probabilité pour que, la valeur moyenne de la densité de probabilité de l'énergie du faisceau incident étant E_0 , on ait, à la profondeur x , l'énergie des particules dans le voisinage de E . Ainsi la fonction

$$h(E_0, E) = g_0(E_0, E, 0)$$

donne le profil en énergie du faisceau incident. Nous supposons que E_0 est toujours très grand devant la largeur de la fonction $h(E_0, E)$. Si l'on définit $g(\hat{E}, E, x)$

comme la densité de probabilité de l'énergie E à la profondeur x sachant que E est égale à $\hat{E}$ pour x égale à zéro, on obtient :

$$g_0(E_0, E, x) = \int_0^\infty h(E_0, \hat{E}) g(\hat{E}, E, x) d\hat{E}$$

$$\text{et } g(\hat{E}, E, 0) = \delta(\hat{E} - E)$$

On peut admettre que dans le voisinage d'un E_0 donné la densité $h(E_0, E)$ ne dépend que de la différence $(E - E_0)$. De plus on peut supposer que cette fonction $h(E - E_0)$ est symétrique autour de la valeur moyenne E_0 ; il vient alors :

$$g_0(E_0, E, x) = \int_0^\infty h(E_0 - \hat{E}) g(\hat{E}, E, x) d\hat{E}$$

que nous écrirons sous la forme d'une convolution :

$$g_0(E_0, E, x) = h(E_0) * g(E_0, E, x) \quad (2)$$

Dans la mesure où l'on étudie $N(E_0)$ au voisinage de l'énergie E_R d'une résonance, on peut supposer que $g(E_0, E, x)$ ne dépend que de $E_0 - E = u$; Ceci revient à ne considérer que des pertes d'énergie u faibles devant E_R et à admettre que les caractéristiques de ralentissement du milieu sont homogènes. La relation (1) devient alors, en tenant compte de (2) :

$$N(E_0) = \int_0^\infty h(E_0) * \left[\sigma_\theta(E) \int_0^\infty g(E_0 - E, x) C(x) dx \right] dE$$

que l'on peut écrire sous la forme :

$$N(E_0) = h(E_0) * \sigma_\theta(E_0) * \int_0^\infty C(x) g(E_0, x) dx$$

On peut considérer la section efficace apparente $\bar{\sigma}_0(E_0)$ définie par

$$\bar{\sigma}_0(E_0) = h(E_0) * \sigma_0(E_0)$$

On a alors :

$$N(E_0) = \bar{\sigma}_0(E_0) * \int_0^\infty g(E_0, x) C(x) dx \quad (3a)$$

qui est identique à :

$$N(E_0) = \int_0^\infty \bar{\sigma}_0(E_0 - u) \left[\int_0^\infty C(x) g(u, x) dx \right] du \quad (3b)$$

d'après l'hypothèse d'homogénéité
Il importe de noter, que la relation 3a ou 3b n'a de sens que dans la mesure où la présence des noyaux dont $C(x)$ est le profil ne perturbe pas les propriétés de la densité $g(u, x)$ caractéristique de la perte d'énergie des particules dans la cible. On pourra appliquer cette relation essentiellement dans deux cas :

i) le noyau considéré est à dilution infinie de sorte que $g(u, x)$ ne dépend que de la matrice.

ii) le noyau considéré est un isotope d'un élément de la cible (par exemple O^{18} dans une cible d'oxyde).

. Dans la pratique on relève expérimentalement les courbes d'excitation respectivement sur une cible très mince (vis à vis de la largeur de la résonance) et sur une cible où le profil $C(x)$ est inconnu ; Il s'agit alors de déterminer à partir de ces courbes le profil $C(x)$. En fait il est plus aisé d'opérer dans le sens inverse, à savoir : calculer la courbe d'excitation théorique pour un profil $C(x)$ donné, connaissant la courbe d'excitation relevée sur une cible mince ; comparer ensuite cette courbe théorique à la courbe expérimentale obtenue. Le calcul implique la connaissance de la fonction $g(u, x)$.

B) Propriétés de $g(u, x)$

1) La fonction $g(u, x)$ est une densité de probabilité sur la variable u . on a donc :

$$\int_0^{\infty} g(u, x) du = 1 \quad (4)$$

De plus la valeur moyenne $\bar{u}$ vaut lorsqu'elle existe :

$$\bar{u} = \int_0^{\infty} u g(u, x) du = \frac{dE}{dx} x \quad (5)$$

où $\frac{dE}{dx}$ est le pouvoir d'arrêt (constant dans le voisinage de E_0 par hypothèse) de la cible pour les particules incidentes.

Notons que : $g(u, 0) = \delta(u)$ (6)

2) On peut considérer les pertes d'énergie u_{x_1} et u_{x_2} dans deux sections successives comme des variables aléatoires indépendantes (hypothèse d'homogénéité). Ainsi la densité de probabilité de la variable $u_{x_1 + x_2}$ définie par :

$$u_{x_1 + x_2} = u_{x_1} + u_{x_2}$$

est donnée par :

$$g(u, x_1 + x_2) = g(u, x_1) * g(u, x_2) \quad (7)$$

Nous dirons que la densité $g(u, x)$ est infiniment divisible (Lukacs). Ainsi la transformée de Laplace $G(p, x)$ de $g(u, x)$ devra satisfaire à :

$$G(p, x_1 + x_2) = G(p, x_1) \cdot G(p, x_2)$$

C'est ainsi que l'on peut donner à $G(p, x)$ la forme générale caractéristique des fonctions infiniment divisibles :

$$G(p, x) = e^{\alpha \psi(p)} \quad (8)$$

où $\psi(0) = 0$

pour satisfaire $G(0, x) = 1$, condition identique à l'équation (4). Notons que la diffusion multiple des particules chargées conduit à des résultats analogues comme le montrent les calculs de Scott.

D'après l'équation (5), on peut écrire alors :

$$\bar{u} = -\alpha \left[\frac{d\psi}{dp} \right]_{p=0}$$

d'où $\psi'(0) = -\frac{dE}{d\alpha}$ (9)

si $\psi(p)$ est dérivable à l'origine

3) Soit $I(u)$ défini par :

$$I(u) = \int_0^\infty g(u, x) dx \quad (10)$$

la transformée de Laplace de $I(u)$ devient pour $\Re(\psi(p)) < 0$

$$\mathcal{L} \langle I(u) \rangle = -\frac{1}{\psi(p)}$$

En appliquant le théorème d'Abel, valable lorsque la limite du premier membre existe :

$$\lim_{u \rightarrow \infty} I(u) = \lim_{p \rightarrow 0} (p \mathcal{L} \langle I(u) \rangle) \quad (11)$$

il vient :

$$\lim_{u \rightarrow \infty} I(u) = \lim_{p \rightarrow 0} \left(-\frac{p}{\psi(p)} \right)$$

Or d'après (9) on peut écrire :

$$\psi(p) = -\frac{dE}{d\alpha} p + o(p) \quad (12)$$

D'où l'on tire le résultat très général suivant :

$$\lim_{u \rightarrow \infty} I(u) = \frac{1}{\frac{dE}{d\alpha}} \quad (13)$$

pourvu que $\bar{u}$ (soit $\psi'(0)$) existe.

C) Propriétés de la courbe d'excitation

1) Effet d'un absorbant

D'après la propriété de $g(u, x)$ d'être infiniment divisible, il est aisé de calculer la courbe d'excita-

tion $N_a(E_0)$ lorsque l'on interpose un absorbant homogène d'épaisseur a , de même nature que la cible, en fonction de la courbe d'excitation $N(E_0)$ obtenue sans absorbant. En effet on a d'après (3a) :

$$N_a(E_0) = \bar{\sigma}_0(E_0) * \int_a^\infty g(E_0, x) dx = \bar{\sigma}_0(E_0) * \int_0^\infty g(E_0, x+a) dx$$

et d'après (7) et (3a) il vient :

$$N_a(E_0) = N(E_0) * g(E_0, a) \quad (14)$$

Cette propriété sera utilisée pour le calcul de la courbe d'excitation en considérant la cible comme constituée d'une série d'absorbants (voir plus bas). En fait cela revient à écrire que le profil de faisceau après l'absorbant est $h(E_0) * g(E_0, a)$.

2) Cible homogène d'épaisseur infinie

. Nous avons donc ici :

$$C(x) = C_0 \quad \forall x \in [0, \infty]$$

La courbe d'excitation $N_\infty(E_0)$ devient :

$$N_\infty(E_0) = \bar{\sigma}(E_0) * I(E_0) C_0 \quad (15)$$

Pour une énergie E_0 grande devant l'énergie E_R et la largeur de la résonance, l'expression (15) tend vers une constante qui est donnée d'après (13) par :

$$N_\infty(E_0) = \int_0^\infty \bar{\sigma}(u) du \cdot \frac{C_0}{\frac{dE}{dx}} \quad (16)$$

Nous pouvons remarquer que l'intégrale $\int_0^\infty \bar{\sigma}(u) du$

est égale à $\int_0^\infty \bar{\sigma}_0(u) du$ et caractérise l'intensité de la résonance. $N_\infty(E_0)$ est appelé le plateau en cible épaisse.

3) Cible homogène d'épaisseur égale à X

Nous avons ici :

$$\begin{cases} C(x) = C_0 & \text{pour } x \in [0, X] \\ C(x) = 0 & \text{ailleurs} \end{cases}$$

Calculons l'intégrale de la courbe d'excitation $N_X(E_0)$ obtenue sur une telle cible ; il vient d'après (3a) et (4)

$$\int_0^\infty N_X(u) du = \int_0^\infty \sigma_\theta(u) du \cdot C_0 X$$

Ainsi d'après (16) on obtient :

$$\frac{\int_0^\infty N_X(u) du}{N_\infty(E_0)} = \frac{dE}{dx} X \quad (17)$$

ce qui correspond à la perte moyenne d'énergie dans la cible considérée. Cette relation très simple et sans aucune hypothèse sur $g(u, x)$ (sinon la divisibilité infinie) est d'une grande utilité. Elle a déjà été établie par Gove. Notons que les limites d'intégration peuvent être remplacées, dans le cas de l'existence relativement proche d'autres résonances, par un intervalle suffisant autour de E_R . Les résonances $E'_R < E_R$ fournissent un "fond" constant.

II. MODELE STOCHASTIQUE DE LA PERTE D'ENERGIE DES PARTICULES DANS LA MATIERE.

A) Formule de Rutherford. Section efficace de collision

. La section efficace de collision (formule de Rutherford) des ions incidents avec les électrons des

atomes de la cible est donnée par :

$$\Phi(u) = \frac{2\pi e^4 z^2}{m v^2} N \rho \frac{Z}{A} \frac{1}{u^2} \quad (18)$$

où z est le nombre de charge élémentaire de la particule incidente

v la vitesse de la particule incidente

m la masse de l'électron

e la charge de l'électron

N le nombre d'Avogadro

ρ la densité de la cible

Z la charge molaire de la cible

A la masse molaire de la cible

u représente l'énergie perdue par la particule incidente lors de la collision. (18) montre que pour la perte d'énergie l'interaction avec les noyaux peut être négligée.

Pour alléger l'écriture, nous poserons :

$$\Phi(u) = K \frac{1}{u^2} \quad (19)$$

[eV⁻¹cm⁻¹] [eV cm⁻¹]

où $K = \frac{z^2}{\beta^2} \frac{m c^2}{[eV]} 2 \frac{B}{[cm^{-1}]}$

La constante B est spécifique de la nature de la cible et vaut :

$$B = \pi r_0^2 N \rho \frac{Z}{A}$$

où $r_0 = \frac{e^2}{m c^2}$ (rayon classique de l'électron)

Le calcul donne :

$$B = 0,150 \frac{Z}{A} \rho$$

[cm⁻¹] [g.cm⁻³]

. Il importe de noter que la relation (18) ne s'applique en principe qu'à des électrons libres. Nous supposerons dans la suite que les électrons des atomes de la cible jouent tous le même rôle quant aux pertes d'énergie.

. Dans le cas d'une collision frontale, il existe une énergie maximum u_{MAX} transférable à l'électron libre :

$$u_{MAX} \approx 4 \frac{m}{M} E_0 = 2 m v^2 = 2 m c^2 \beta^2 \quad (20)$$

où M est la masse de l'ion incident.

Notons que nous sommes dans le cas non relativiste ($E_0 \ll M c^2$) et nous avons :

$$\beta^2 = \frac{2 E_0}{M c^2}$$

. Nous considérerons ici le cas où $\Phi(u)$ est intégrable ; il convient alors de se fixer un seuil d'énergie minimum u_{min} de telle sorte que

$$\Phi(u) = 0 \text{ pour } 0 < u < u_{min}$$

Cette énergie u_{min} sera considérée comme la même pour tous les électrons de l'atome constituant la cible. Notons qu'alors

$m = \int_{u_{min}}^{u_{max}} \Phi(u) du$ est le nombre d'interactions par unité de longueur dans la cible ; m est donc fini selon nos hypothèses.

B) Modèle stochastique

. Soit $f(u)$ la densité de probabilité (spectre d'interaction primaire) pour qu'une particule perde au cours d'une interaction l'énergie u . $f(u)$ est définie à partir de la section efficace de collision $\Phi(u)$ par la relation

$$f(u) = \frac{\Phi(u)}{m} \quad (21)$$

où m vaut :

$$m = K \left[\frac{1}{u_{min}} - \frac{1}{u_{max}} \right] \quad (22)$$

$f(u)$ est exprimé en eV^{-1} . Nous appelons $\lambda = \frac{1}{m}$ le libre parcours moyen des particules incidentes.

. Ainsi dans la mesure où toutes les interactions (ion - électron) sont des événements isolés en nombre fini, on peut, comme on l'a vu plus haut, considérer une perte d'énergie u à la profondeur x comme la somme de n variables aléatoires indépendantes u_i ayant toutes la même densité de probabilité $f(u)$:

$$u = \sum_{i=1}^n u_i \quad (23)$$

Il découle des hypothèses (indépendance) que le nombre n d'interactions est une variable aléatoire qui suit la distribution de Poisson (axiome de Poisson, Blanc - Lapierre) dont la valeur moyenne n est donnée par :

$$\bar{n} = mx$$

à condition de négliger la diffusion angulaire du faisceau incident (c'est à dire que la direction des particules reste parallèle à l'axe des x), ce qui est bien vérifié dans ce problème.

On obtient alors la densité de probabilité $g(u, x)$ par la relation :

$$g(u, x) = \sum_{n=0}^{\infty} P_n(x) f(u)^{*n} \quad (24)$$

où
$$P_n(x) = \frac{e^{-mx} (mx)^n}{n!}$$

et
$$f(u)^{*0} = \delta(u)$$

1) Calcul des trois premiers moments centrés de la densité $g(u, x)$

Pour ce faire, il est commode de prendre la transformée de Laplace de l'équation (24). Nous poserons :

$$G(p, x) = \int_0^{\infty} g(u, x) e^{-pu} du \quad (25)$$

$$\bar{F}(p) = \int_0^{\infty} f(u) e^{-pu} du \quad (26)$$

Il vient alors :

$$G(p, x) = \sum_{n=0}^{\infty} \frac{e^{-mx} (mx)^n}{n!} \bar{F}(p)^n$$

d'où

$$G(p, x) = e^{-mx} \sum_{n=0}^{\infty} \frac{(mx \bar{F}(p))^n}{n!}$$

On obtient donc la fonction caractéristique d'une loi de Poisson composée :

$$G(p, x) = e^{mx[F(p)-1]} \quad (27)$$

On vérifie bien que $g(u, x)$ est normé car $G(0, x) = 1$.

De plus nous pouvons remarquer que l'expression (27) est bien de la forme donnée par la relation (3) caractérisant une densité de probabilité infiniment divisible.

. Pour le calcul des trois premiers moments centrés, nous appliquons la relation suivante :

$$\mu_n = (-1)^n \left[\frac{d^n}{dp^n} [\text{Log } G(p, x)] \right]_{p=0} \quad (28)$$

soit encore :

$$\mu_n = (-1)^n \left[\frac{d^n}{dp^n} \bar{F}(p) \right]_{p=0} \cdot mx$$

On obtient alors :

$$\left. \begin{aligned} \mu_1 &= -\bar{F}'(0) mx = mx \int u f(u) du = x \int u \tilde{f}(u) du \\ \mu_2 &= \bar{F}''(0) mx = mx \int u^2 f(u) du = x \int u^2 \tilde{f}(u) du \\ \mu_3 &= -\bar{F}'''(0) mx = mx \int u^3 f(u) du = x \int u^3 \tilde{f}(u) du \end{aligned} \right\} \quad (29)$$

. Comme nous l'avons vu plus haut, le premier

moment μ_1 est parfaitement déterminé puisqu'il représente la perte moyenne d'énergie à la profondeur x .

$$\mu_1 = \frac{dE}{dx} \propto \quad (30)$$

La connaissance du pouvoir d'arrêt $\frac{dE}{dx}$ va nous permettre de fixer le paramètre $u_{\min}$, non déterminé jusqu'à présent. Il vient d'après (19) (29) et (30) :

$$\frac{dE}{dx} = K \text{ Log } \frac{u_{\max}}{u_{\min}} \quad (31)$$

Il importe de souligner que la détermination de $u_{\min}$ par cette méthode est purement artificielle ; la valeur de $u_{\min}$ ainsi trouvée n'a pas de signification physique. Nous verrons dans la suite que nous pourrions donner à $u_{\min}$ d'autres valeurs si l'on décompose la perte d'énergie en pertes dues à des collisions distantes, non dénombrables et non dispersives et en pertes dues à des collisions frontales qui suivent le modèle stochastique proposé et qui sont en nombre fini par unité de longueur et qui donnent lieu à une dispersion en énergie.

. Il convient de noter ici que la formule de Bethe donnant le pouvoir d'arrêt s'écrit :

$$\frac{dE}{dx} = 2 K \text{ Log } \frac{u_{\max}}{I(Z)} \quad (32)$$

où $I(Z)$ est le potentiel moyen d'ionisation des atomes de la cible. La définition de $u_{\min}$ correspond donc en fait à

$$u_{\min} = \frac{I^2(Z)}{u_{\max}} = \frac{I^2(Z)}{2mc^2\beta^2} \quad (33)$$

. Le second moment μ_2 représente le carré de l'écart standard σ . On obtient d'après (29) et (19)

$$\sigma = \sqrt{\mu_2} = \sqrt{K(u_{\max} - u_{\min})} \cdot \sqrt{cx} \quad (34)$$

que nous écrirons :

$$\sigma = S \sqrt{cx} \quad (35)$$

Si l'on néglige $u_{\min}$ devant $u_{\max}$, il vient :

$$\sigma = 2 mc^2 z \sqrt{0,15 \frac{Z}{A} \rho x}$$

ce qui donne l'expression connue de l'effet de "straggling" :

$$\sigma = 8,85 z \sqrt{\frac{2Z}{A}} \sqrt{\rho x} \quad (36)$$

[keV] [mg cm⁻²]

Il est bon de remarquer que le coefficient S est en première approximation (si $u_{\min} \ll u_{\max}$) indépendant de l'énergie des particules. On devrait s'attendre à obtenir sur les noyaux lourds un coefficient de straggling plus faible que 8,85, en raison des électrons fortement liés des couches profondes de l'atome qui contribuent à augmenter la valeur de $u_{\min}$ d'après la relation (33).

. On obtient pour le moment centré d'ordre 3, en négligeant $u_{\min}$ devant $u_{\max}$:

$$\mu_3 = K \frac{u_{\max}^2}{1} x$$

Le fait que μ_3 soit toujours positif prouve que la densité $g(u, x)$ présente une "queue" pour les pertes u supérieures à $u_{\max}$. En fait on peut caractériser la dissymétrie de la densité $g(u, x)$ par le coefficient sans dimension D :

$$D = \frac{\mu_3}{\mu_2^{3/2}} = \frac{u_{\max}}{2(K u_{\max} x)^{1/2}}$$

qui s'écrit encore :

$$D = \frac{u_{\max}}{2 \times 8,85 z \sqrt{\frac{2Z}{A}} \sqrt{\rho x}} \quad (37)$$

[keV] [mg cm⁻²]

Le coefficient de dissymétrie D décroît avec la racine carrée de l'épaisseur ; la densité $g(u, x)$ tend vers la symétrie pour des profondeurs x telles que la perte u soit grande devant $u_{\max}$. Notons que le coefficient D dépend de l'énergie des particules par l'intermédiaire de $u_{\max}$.

2) Cible homogène d'épaisseur infinie

Il convient de calculer $I(u)$ défini par l'équation (10) où $g(u, x)$ a la forme donnée par (24) ; on obtient :

$$I(u) = \sum_{n=0}^{\infty} \left[f(u)^{\frac{x^n}{n!}} \cdot \int_0^{\infty} \frac{e^{-mx} (mx)^n}{n!} dx \right]$$

qui donne :

$$I(u) = \frac{1}{m} \sum_{n=0}^{\infty} f(u)^{\frac{x^n}{n!}} \quad (38)$$

Ce résultat est d'une grande importance car il montre nettement le rôle que joue $u_{\min}$, soit la forme exacte de $f(u)$, sur l'allure de $I(u)$ pour u voisin de 0. On voit de plus que $I(u)$ présente une composante δ à l'origine. Ce résultat se traduit expérimentalement par une suroscillation (Bondelid et Butler) de $N(E_0)$ au voisinage de l'énergie de la résonance (effet Lewis)

La transformée de Laplace de $I(u)$ est donnée par :

$$\mathcal{L}\langle I(u) \rangle = \int_0^{\infty} e^{-mx} [F(p)-1] dx$$

$$\mathcal{L}\langle I(u) \rangle = \frac{1}{m[F(p)-1]} \left[e^{-mx[F(p)-1]} \right]_0^{\infty} \quad (39)$$

On peut montrer que pour $\Re(p) > a > 0$ on a $|F(p)| < 1$

en effet :

$$F(p) = \int_0^{\infty} e^{-pu} f(u) du = \int_0^{\infty} e^{-au} e^{-ibu} f(u) du$$

d'où

$$|F(p)| < \int_0^{\infty} e^{-au} f(u) du < \int_0^{\infty} f(u) du = 1$$

On obtient ainsi :

$$\mathcal{L}\langle I(u) \rangle = \frac{1}{m[1-F(p)]} = \frac{1}{m} \sum_{n=0}^{\infty} F(p)^n \quad (40)$$

Ce qui est bien la transformée de (38).

En appliquant l'équation (41), on retrouve bien la valeur de la limite de $I(u)$ quand u tend vers l'infini (équation 15) :

$$\lim_{u \rightarrow \infty} I(u) = \lim_{p \rightarrow 0} \frac{p}{m[1-F(p)]} = \frac{1}{-m F'(0)}$$

$$\text{soit : } \lim_{u \rightarrow \infty} I(u) = \frac{1}{\frac{1}{m} \frac{dF}{du}}$$

La valeur de cette limite nous permettra de vérifier les calculs effectués sur machine.

Il est intéressant de considérer la fonction $J(u)$ défini

$$\text{par : } J(u) = I(u) - \frac{1}{\frac{1}{m} \frac{dF}{du}} Y(u)$$

où $Y(u)$, est la fonction échelon unité $Y(u) = 1$ pour $u > 0$
 $Y(u) = 0$ pour $u \leq 0$

$J(u)$ tend vers 0 pour u tendant vers l'infini.

On obtient la transformée de Laplace de $J(u)$:

$$\mathcal{L}\langle J(u) \rangle = \frac{1}{m[1-F(p)]} - \frac{1}{m F'(0)p}$$

On peut calculer ainsi l'intégrale de $J(u)$:

$$\int_{-\infty}^{+\infty} J(u) du = \lim_{p \rightarrow 0} \mathcal{L}\langle J(u) \rangle = \frac{F(0)}{2m[F'(0)]^2}$$

D'après (29), (30) et (34), il vient :

$$\int_{-\infty}^{+\infty} J(u) du = \frac{1}{2} \frac{S^2}{\left(\frac{1}{m} \frac{dF}{du}\right)^2}$$

Cette quantité est homogène à une longueur ; elle correspond comme nous le verrons plus loin (72) à $\frac{x_0}{2}$ et exprime l'excès de $I(u)$ par rapport à $Y(u)$ (effet Lewis) de façon plus quantitative. Nous ne pousserons pas plus loin ici l'analyse de $J(u)$.

3) Cible homogène d'épaisseur égale à X

Il s'agit de calculer :

$$I_X(u) = \int_0^X g(u, x) dx \quad (41)$$

En prenant la transformée de Laplace, il vient d'après (40)

$$\mathcal{L}\langle I_X(u) \rangle = \frac{1}{m[1-F(u)]} \left[1 - e^{-mX[1-F(u)]} \right] \quad (42)$$

d'où l'on déduit :

$$I_X(u) = I(u) - I(u) * g(u, X) \quad (43)$$

On peut aussi expliciter $g(u, x)$ dans l'équation (41), il vient alors :

$$I_X(u) = \frac{1}{m} \left[\sum_{n=0}^{\infty} f(u)^{m^n} - \sum_{n=0}^{\infty} K_n(X) f(u)^{m^n} \right] \quad (44)$$

$$\text{où } K_n(X) = \int_0^X \frac{t^n e^{-t}}{n!} dt$$

En intégrant par parties, il vient :

$$K_n(X) = \sum_{p=0}^n \frac{e^{-mX} (mX)^p}{p!}$$

On peut remarquer que la suite des $K_n(X)$ représente la fonction de répartition de la distribution de probabilité de Poisson.

On peut écrire la relation (44) sous la forme :

$$I_X(u) = \frac{1}{m} \sum_{n=0}^{\infty} K_n(X) f(u)^{m^n}$$

où $\bar{K}_n(x) = 1 - K_n(x)$

On voit que K_n tend vers 0 quand n tend vers l'infini si X est fini. De plus on démontre la relation :

$$mX = \sum_{n=0}^{\infty} \bar{K}_n(x)$$

Il ressort de ceci que l'on peut considérer :

$$\frac{f_X(u)}{X} = \sum_{n=0}^{\infty} \frac{\bar{K}_n(x)}{mX} f(u)^{m \cdot n}$$

comme la densité de probabilité de la variable u définie comme la somme de n variables aléatoires indépendantes u_i :

$$u = \sum_{i=1}^n u_i$$

où n suit la densité de probabilité $\frac{\bar{K}_n(x)}{mX}$

Cette remarque est fort utile pour un calcul par la méthode de Monte-Carlo.

4) Cible ayant pour profil $C(x) \neq$ Constante

Il s'agit de calculer, pour un profil $C(x)$ donné, l'intégrale suivante :

$$H(u) = \int_0^{\infty} C(x) g(u, x) dx \quad (45)$$

qui devient d'après (24) :

$$H(u) = \sum_{n=0}^{\infty} \left[f(u)^{m \cdot n} \int_0^{\infty} C(x) \frac{e^{-mx} (mx)^n}{n!} dx \right]$$

On peut écrire $H(u)$ sous la forme :

$$H(u) = \sum_{n=0}^{\infty} S_n(m) \frac{m^n}{n!} f(u)^{m \cdot n} \quad (46)$$

où

$$S_n(m) = \int_0^{\infty} C(x) x^n e^{-mx} dx$$

On voit que l'on peut considérer les coefficients $S_n(m)$ soit comme les moments d'ordre n de la fonction $(C(x)e^{-mx})$, soit comme la transformée de Laplace de $(x^n C(x))$ qui correspond à $(-1)^n \frac{d^n}{dx^n} [C(x)]$. Ainsi pour des profils $C(x)$ ayant une forme analytique simple, il sera relativement aisé de déterminer les coefficients $S_n(m)$ et de calculer la série de la relation (46).

5) Approximations pour le modèle stochastique

Il apparaît, dans ce modèle, que la valeur de u_{min} trouvée d'après l'équation (31) est généralement très faible (environ 10 eV). Ceci entraîne que le nombre d'interactions m par unité de longueur est élevé, ce qui conduit, pour le calcul de $g(u,x)$, à considérer un grand nombre d'interactions. Afin d'alléger les calculs, il est apparu souhaitable d'introduire une approximation qui consiste à distinguer, pour la perte d'énergie, deux types de collisions :

- des collisions que l'on considère comme distantes, qui donnent lieu à une perte continue d'énergie sans aucune dispersion
- des collisions frontales, en nombre fini par unité de longueur, qui donnent lieu à une perte d'énergie avec une dispersion.

Soit l le nombre de collisions frontales par unité de longueur et soit k la perte d'énergie par unité de longueur due aux collisions distantes. Nous posons arbitrairement, par exemple :

$$k = \frac{1}{2} \frac{dE}{dx} \quad (47)$$

On peut définir la densité $\bar{g}(u,x)$, due aux collisions purement stochastiques, en fonction de la densité $g(u,x)$ comprenant tous les types d'interactions par la relation :

$$g(u,x) = \bar{g}(u-kx, x) \quad (48)$$

La transformée de Laplace de cette densité devient :

$$G(p,x) = G(p-kx, 0) \quad (49)$$

La densité $g(u,x)$ est normée car $G(0,x)$ est égale à l'unité ; de plus on obtient pour les moments centrés :

$$\mu_1 = \alpha \left[k + (-l F'(0)) \right] = \frac{dE}{d\alpha} \propto$$

d'où on tire (pour $k \neq \frac{dE}{d\alpha} / 2$) :

$$\frac{dE}{d\alpha} = 2K \text{Log} \frac{u_{\text{max}}}{u_{\text{min}}} \quad (50)$$

Cette équation définit $\bar{u}_{\text{min}}$ dont la valeur typiquement de l'ordre de 150 eV est d'un ordre de grandeur supérieur à la valeur de u_{min} trouvée dans la théorie précédente. Les deuxième et troisième moments centrés restent inchangés (en première approximation).

. Dans cette approximation, le nombre d'interactions 1 par unité de longueur est peu élevé et il est alors aisé de calculer la série :

$$\bar{g}(u, \alpha) = \sum_{n=0}^{\infty} \frac{e^{-l\alpha} (l\alpha)^n}{n!} f(u)^{*n}$$

On obtient la véritable densité de probabilité $g(u, x)$ en effectuant sur la fonction $\bar{g}(u, x)$ ainsi trouvée une translation égale à kx vers les énergies croissantes :

$$g(u, \alpha) = \sum_{n=0}^{\infty} \frac{e^{-l\alpha} (l\alpha)^n}{n!} f(u - k\alpha)^{*n} \quad (51)$$

. Dans le cas de la cible infinie, le calcul de $I(u)$ défini par (10) devient dans cette approximation :

$$I(u) = \sum_{n=0}^{\infty} \int_0^{\infty} f(u - k\alpha)^{*n} \frac{e^{-l\alpha} (l\alpha)^n}{n!} d\alpha$$

En prenant les transformées de Laplace, il vient :

$$\mathcal{L} \langle I(u) \rangle = \frac{1}{kp + l - l F(p)}$$

$$\mathcal{L} \langle I(u) \rangle = \frac{1/k}{p + l/k} \sum_{n=0}^{\infty} \left[\frac{l/k}{p + l/k} F(p) \right]^n$$

D'où l'on déduit (sur l'axe $u \in [0, \infty]$) :

$$I(u) = \frac{1}{k} e^{-u \frac{1}{k}} * \sum_{n=0}^{\infty} \left[\frac{1}{k} e^{-u \frac{1}{k}} * f(u) \right]^{*n} \quad (52)$$

En comparant l'équation (52) à l'équation (38), tout se passe comme si on prenait au lieu de $f(u)$ une nouvelle fonction d'interaction égale à $\frac{1}{k} e^{-u \frac{1}{k}} * f(u)$

et que l'on convole le résultat de l'équation (38) par $\frac{m}{k} e^{-u \frac{1}{k}}$.

C) Méthodes de calcul de $g(u, x)$

1) Méthode directe

La méthode consiste en premier lieu à calculer la suite $f(u)^{*n}$ des autoconvolées successives de $f(u)$. Un programme, mis au point par Sauce, effectue ce travail ; le calcul s'arrête dès que la convergence vers la gaussienne est atteinte. On peut alors calculer :

$$g(u, x) = \sum_{n=0}^{\infty} \frac{e^{-mx} (mx)^n}{n!} f(u)^{*n} \quad (53)$$

$$\text{et } I(u) = \frac{1}{m} \sum_{n=0}^{\infty} f(u)^{*n} \quad (54)$$

On effectue le calcul de la série (53) jusqu'à ce que le coefficient de Poisson $P_n(x)$ devienne négligeable. Pour le calcul de la série (54), on s'arrête dès que la limite $I(u) = \frac{1}{m} \frac{dI}{dx}$ pour u tendant vers l'infini est atteinte.

2) Méthode de Monte-Carlo

. Il est facile d'engendrer sur une calculatrice une variable aléatoire x de densité de probabilité $f(x)$ donnée. On utilise pour cela un sous programme qui génère des nombres aléatoires $R \in [0, 1]$ de densité

uniforme sur cet intervalle. Soit $F(x)$ la fonction de répartition de la densité $f(x)$ défini par :

$$F(x) = \int_0^x f(t) dt$$

Il est facile de montrer que la variable aléatoire x définie par :

$$x = F^{-1}(R)$$

où F^{-1} est la fonction inverse de la fonction de répartition et R la variable aléatoire définie plus haut, possède la densité de probabilité $f(x) = \frac{dF}{dx}$

. La méthode, pour rechercher la solution $g(u, x)$, consiste à effectuer la somme :

$$u = \sum_{i=1}^n u_i$$

des n variables aléatoires indépendantes u de densité $f(u)$, le nombre n étant lui-même une variable aléatoire discrète de densité $p_n(x) = \frac{e^{-mx}(mx)^n}{n!}$. On effectue cette

somme N fois (N événements) en conservant en mémoire les N valeurs $(u(1), u(2), \dots, u(N))$ des u ainsi trouvées. Nous obtenons alors la densité $g(u, x)$ par la relation :

$$g(u, x) = \frac{1}{N \cdot \Delta u} \left[\begin{array}{l} \text{Nb des } u(i) \in [u, u+\Delta u] \\ \text{pour tous les } i \in [1, N] \end{array} \right] \quad (55)$$

Pour engendrer la variable aléatoire u de densité $f(u)$ donné par :

$$f(u) = \frac{u_{\max} - u_{\min}}{u_{\max}^2 - u_{\min}^2} \cdot \frac{1}{u^2} \quad \text{pour } u \in [u_{\min}, u_{\max}] \quad (56)$$

On calcule la fonction de répartition $F(u)$:

$$F(u) = \frac{u_{\max} - u_{\min}}{u_{\max}^2 - u_{\min}^2} \left[\frac{1}{u_{\min}} - \frac{1}{u} \right]$$

D'où l'on tire u en fonction de la variable aléatoire R

$$u = \frac{u_{\max} u_{\min}}{(1-R) u_{\max} + R u_{\min}} \quad (57)$$

Les valeurs de u trouvées par la relation (57) ont la densité de probabilité $f(u)$ donné par (56). Il s'agit ensuite d'engendrer des nombres entiers n aléatoires suivant la distribution de Poisson :

$$P_n(x) = \frac{e^{-mx} (mx)^n}{n!} \quad (58)$$

On calcule la suite des $T_n(x)$ définie par :

$$T_n(x) = \sum_{i=0}^n P_i(x) \quad (59)$$

Il suffit de mener le calcul jusqu'à la valeur de $n \approx 3 mx$. On tire alors le nombre aléatoire R de densité uniforme sur l'intervalle $[0,1]$ et l'on cherche la valeur de n telle que l'on ait la condition :

$$T_{n-1} < R < T_n \quad (60)$$

Le nombre aléatoire n ainsi trouvé suit la distribution $P_n(x)$ donné par (58).

. La figure 1 montre l'allure de la fonction $g(u,x)$ calculée par cette méthode. En raison de la nature statistique de la méthode de calcul, les résultats présentent des erreurs ; on peut diminuer l'importance relative de ces erreurs en augmentant le nombre N d'événements ce qui augmente le temps de calcul sur la machine.

. Le calcul de $I(u)$ donné par (45) est relativement simple à effectuer par cette méthode. Nous écrivons en fait $I(u)$ en séparant la composante ξ :

$$I(u) = \frac{S(u)}{m} + \frac{1}{m} \sum_{i=1}^m \tilde{f}(u)^{u_i} \quad (61)$$

Il s'agit de calculer alors la somme des variables aléatoires u_i (de densité de probabilité $f(u)$) pour N événements :

$$u_n = \sum_{i=1}^n u_i$$

où n prend toutes les valeurs entières de 1 à 10 par exemple. Ainsi la suite $\{u_1(1) \dots u_1(N)\}$ a pour densité $N f(u)$, la suite $\{u_2(1) \dots u_2(N)\}$ a pour densité $N f(u)$ etc... L'ensemble de la suite des $u_j(i)$ pour $j \in [1, 10]$ et $i \in [1, N]$ a donc pour densité $N \sum_{n=1}^{10} f(u)^{*n}$. Nous aurons donc pour la partie fonctionnelle de $I(u)$: $\tilde{I}(u)$

$$\tilde{I}(u) = \frac{1}{m N \Delta u} \left\{ \begin{array}{l} \text{Nb des } u_j(i) \in [u, u + \Delta u] \\ \forall j \in [1, 10] \\ \forall i \in [1, N] \end{array} \right\} \quad (62)$$

La relation (11) donnant :

$$\lim_{u \rightarrow \infty} \tilde{I}(u) = \frac{1}{\frac{dE}{d\omega}}$$

permet de vérifier si le nombre maximum de 10 interactions que nous avons choisi pour ce calcul est suffisant.

3) Inversion de la transformée de Laplace

Pour alléger l'écriture, nous écrirons :

$$a = u_{\min}$$

$$b = u_{\max}$$

$$\text{d'où : } m = K \left(\frac{1}{a} - \frac{1}{b} \right)$$

a) Détermination de la transformée de Laplace $F(p)$ de $f(u)$

Les tables donnent (Handboock of Mathematical functions)

$$\mathcal{L} \left\langle \frac{1}{(x+\alpha)^2} \right\rangle = \frac{1}{\alpha} + p e^{p\alpha} E_i(-\alpha p)$$

pour $\alpha > 0$

d'où l'on tire :

$$\mathcal{L} \left\langle \frac{1}{\alpha^2} \right\rangle = \frac{e^{-\alpha p}}{\alpha} + p E_i(-\alpha p)$$

pour $x \gg \alpha > 0$ et zéro pour $x < \alpha$

$$\text{Or } f(u) = \frac{K}{m} \frac{1}{u^2} \quad \text{pour } a \leq u \leq b$$

Ceci peut encore s'écrire :

$$f(u) = \frac{K}{m} \left[\underbrace{\frac{1}{u^2}}_{\text{pour } u > a} - \underbrace{\frac{1}{u^2}}_{\text{pour } u > b} \right]$$

d'où l'on déduit la transformée $F(p)$

$$F(p) = \frac{K}{m} \left[\frac{e^{-ap}}{a} - \frac{e^{-bp}}{b} + p [E_i(-ap) - E_i(-bp)] \right]$$

Le développement en série de $E_i(x)$ donne :

$$E_i(x) = \gamma + \text{Log } x + \sum_{n=1}^{\infty} \frac{x^n}{n \cdot n!}$$

où γ est la constante d'Euler

Il vient alors :

$$F(p) = \frac{K}{m} \left[\frac{e^{-ap}}{a} - \frac{e^{-bp}}{b} + p \log\left(\frac{a}{b}\right) + p \sum_{n=1}^{\infty} \frac{b^n - a^n}{n \cdot a^n} p^n \right] \quad (63)$$

Remarquons que d'après (29), on trouve

$$\mu_1 = - F'(0) m \alpha = K \alpha \log\left(\frac{a}{b}\right) \quad (64)$$

$$\text{et } \mu_2 = F''(0) m \alpha = K (b-a) \alpha$$

en accord avec (30) et (34)

b) Détermination de $g(u, x)$ à partir de $G(p, x)$

Nous avons vu précédemment, d'après les équations (22) et (31), que la valeur donnée à $u_{\min}$ joue un rôle prépondérant sur la détermination de la valeur du nombre d'interaction n par unité de longueur et du premier moment $\mu_1 = \bar{u}$; en revanche la valeur des autres moments est peu dépendante de la valeur de $u_{\min}$. Ainsi le fait de faire tendre $u_{\min}$ vers zéro entraîne que le nombre d'interaction par unité de longueur est infini et que la valeur moyenne de u diverge ; néanmoins les autres moments centrés restent, en première approximation, inchangés. Comme, en fait, c'est la forme de $g(u, x)$ autour de sa valeur moyenne que l'on étudie, il est utile de "recadrer" cette fonction autour de sa valeur moyenne (laquelle résulte d'un calcul formé sur la mécanique quantique). C'est pourquoi nous effectuons le changement de variable $\xi = u - \bar{u}$

$$\text{où } \bar{u} = \frac{dF}{dx} x = Kx \log \frac{1}{x}$$

Nous définissons alors la nouvelle densité de probabilité $g_0(\xi, x)$ par :

$$g_c(\varepsilon, x) = g(\varepsilon + \bar{u}, x) \quad (65)$$

et sa transformée de Laplace

$$G_c(p, x) = e^{mx[F(p)-1] + \bar{u}p} \quad (66)$$

En portant la valeur de $F(p)$ calculée en (63) et les valeurs explicites de m et de $\bar{u}$ dans (66), on obtient :

$$G_c(p, x) = \exp \left[K\alpha \left(\frac{e^{-ap}-1}{a} - \frac{e^{-bp}-1}{b} + p \sum_{n=1}^{\infty} \frac{(a)^n - (b)^n}{n \cdot n!} p^n \right) \right]$$

Grâce à cette opération de "recadrage", on peut alors effectuer l'approximation $a_{\min} = a \rightarrow 0$. On obtient alors :

$$G_c(p, x) = \exp \left[K\alpha \left(-p - \frac{e^{-bp}-1}{b} + p \sum_{n=1}^{\infty} \frac{-(b)^n}{n \cdot n!} p^n \right) \right]$$

La formule d'inversion permet de déterminer $g_c(\varepsilon, x)$ par :

$$g_c(\varepsilon, x) = \frac{1}{2\pi i} \int_{-i\infty}^{+i\infty} G_c(p, x) e^{pe} dp$$

Si l'on pose $p = it$, on obtient :

$$g_c(\varepsilon, t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{J(t)} dt \quad (67)$$

où

$$J(t) = K\alpha t \left[\frac{1 - \cos bt}{bt} - S_1(bt) \right] + it \left[\varepsilon - K\alpha \left(1 - \frac{\sin bt}{bt} + \Psi(bt) \right) \right] \quad (68)$$

Les fonctions transcendentes $S_1(x)$ et $\Psi(x)$ bien connues (Handbook of Mathematical functions) sont définies par :

$$S_i(x) = \int_0^x \frac{\sin t}{t} dt$$

$$\psi(x) = C_i(x) - \gamma - \text{Log } x = \int_0^x \frac{\cos t - 1}{t} dt$$

et admettent pour développement :

$$S_i(x) = \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)(2n+1)!}$$

$$\psi(x) = \sum_{n=1}^{\infty} \frac{(-1)^n x^{2n}}{2n \cdot (2n)!}$$

Comme la partie réelle de $J(t)$ (68) est paire par rapport à t et la partie imaginaire impaire, l'expression (67) s'écrit, en posant $\rho = bt$ et $X = X \frac{x}{b}$:

$$g_c(\varepsilon, x) = \frac{1}{\pi u_{\max}} \int_0^{\infty} e^{-\rho X I_1(\rho)} \cos \left[\rho \left(\frac{\varepsilon}{u_{\max}} - X I_2(\rho) \right) \right] d\rho \quad (69)$$

où $I_1(\rho)$ vaut

$$I_1(\rho) = S_i(\rho) - \frac{1 - \cos \rho}{\rho}$$

et $I_2(\rho)$ vaut

$$I_2(\rho) = \psi(\rho) + \frac{\rho - \sin \rho}{\rho^2}$$

Notons que le fait que $I_2(\rho)$ diverge à l'infini comme $\log \rho$ ne gêne pas le calcul de l'intégrale de l'équation (61) car $I_2(\rho)$ figure dans le $\cos$. Par ailleurs $I_1(\rho)$ converge vers une constante ($= \frac{1}{2}$) pour ρ tendant vers l'infini, il est ainsi aisé de calculer cette intégrale sans donner à ρ de trop fortes valeurs. L'élaboration du programme de calcul de cette intégrale est actuellement en cours ; il sera fort intéressant de

comparer $g(u,x)$ trouvé par ce calcul à $g(u,x)$ trouvé par les autres méthodes (Monte-Carlo ou calcul des autoconvolées).

D) Approximations pour $g(u,x)$: Recherche de formes analytiques.

1) Densité de probabilité Gaussienne

Si l'on considère de fortes valeurs de x , on peut montrer que $g(u,x)$ tend vers la loi de Gauss. En effet on peut toujours écrire :

$$x = n\varepsilon \text{ où } \varepsilon \text{ est fini et } n \text{ grand}$$

D'après l'équation (7), qui illustre une propriété essentielle de $g(u,x)$ (noyau infiniment divisible), on obtient :

$$g(u,x) = g(u,\varepsilon)^n$$

Or d'après le théorème de la limite centrale, on voit que, pour n grand, $g(u,x)$ sera voisin d'une loi de Gauss dont la moyenne $\bar{u}$ et l'écart standard σ sont donnés d'après (30) et (35) par :

$$\bar{u} = \mu_1 = \frac{dE}{d\varepsilon} \varepsilon$$

$$\sigma = \sqrt{\mu_2} = S \sqrt{\varepsilon}$$

La fonction $g(u,x)$ pourra donc s'écrire :

$$g(u,x) = \frac{1}{S \sqrt{2\pi\varepsilon}} \exp - \frac{\left(u - \frac{dE}{d\varepsilon} \varepsilon\right)^2}{2 S^2 \varepsilon} \quad (70)$$

Nous verrons dans la suite que cette forme analytique de $g(u,x)$ peut convenir dans de nombreux cas. On voit que cette approximation est mauvaise pour les faibles valeurs de x car la fonction $g(u,x)$ s'étend sur les valeurs de u négatives, ce qui est physiquement impossible. Ceci provient de ce que la gaussienne est symétrique alors que l'on sait que la fonction réelle $g(u,x)$ est pour les faibles valeurs de x fortement dissymétrique (d'après l'équation (37))

. Il est utile pour la suite des calculs de définir l'énergie u_0 et l'épaisseur x_0 telles que la perte moyenne d'énergie u_0 dans l'épaisseur x_0 soit égale à l'écart type de $g(u, x_0)$. On obtient alors la relation :

$$u_0 = \frac{dE}{d\alpha} x_0 = S \sqrt{x_0}$$

$$\text{d'où} \quad x_0 = \frac{u_0^2}{\left(\frac{dE}{d\alpha}\right)^2} \quad (71)$$

$$\text{et} \quad x_0 = \frac{S^2}{\left(\frac{dE}{d\alpha}\right)^2} \quad (72)$$

. Nous dirons donc que l'approximation gaussienne sera d'autant meilleure que x est grand devant x_0 . L'ordre de grandeur de x_0 est de 50 Å typiquement.

. La transformée de Laplace $G(p, x)$ pour la densité de probabilité gaussienne s'écrit :

$$G(p, x) = e^{-\frac{1}{2} \left[\frac{dE}{d\alpha} p + \frac{S^2}{2} p^2 \right]} \quad (73)$$

Il est intéressant, pour cette approximation gaussienne, de calculer $I(u)$ correspondant à la cible d'épaisseur infinie. Il vient d'après (27), (40) et (73) :

$$\mathcal{L} \langle I(u) \rangle = \frac{1}{p \left[\frac{dE}{d\alpha} - \frac{S^2}{2} p \right]} = \frac{2}{S^2} \frac{1}{p} \frac{1}{\left[\frac{2 \frac{dE}{d\alpha}}{S^2} - p \right]}$$

Or d'après (71), ceci donne :

$$\mathcal{L} \langle I(u) \rangle = \frac{2}{u_0 \frac{dE}{d\alpha}} \frac{1}{p} \frac{1}{\left[\frac{2}{u_0} - p \right]} \quad (74)$$

Il vient alors :

$$I(u) = \frac{2}{u_0 \frac{dE}{dx}} \int_{-\infty}^{+\infty} Y(u-v) e^{-\frac{2|v|}{u_0}} Y(-v) dv$$

ce qui donne :

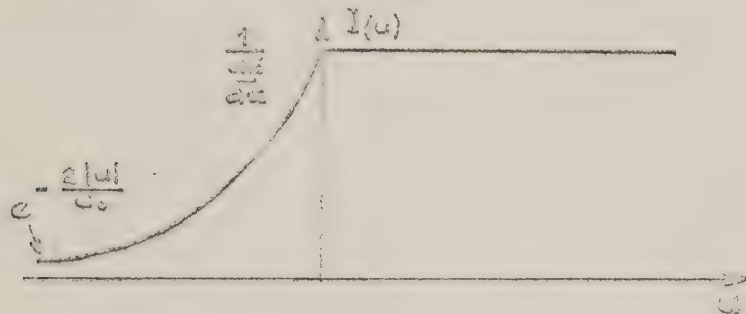
$$I(u) = \frac{2}{u_0 \frac{dE}{dx}} \int_{-\infty}^u e^{-\frac{2|v|}{u_0}} Y(-v) dv$$

ainsi on obtient :

$$I(u) = \frac{1}{\frac{dE}{dx}} e^{-\frac{2|u|}{u_0}} \quad \text{pour } u < 0$$

$$I(u) = \frac{1}{\frac{dE}{dx}} \quad \text{pour } u \geq 0$$

$I(u)$ a l'allure suivante :



Le fait que $I(u)$ s'étende vers des valeurs de u négatives découle des observations faites précédemment sur la validité de l'approximation gaussienne pour $g(u, x)$.

. Nous pouvons remarquer que l'intégrale

$$\int_{-\infty}^{+\infty} J(u) du \quad \text{où } J(u) \text{ est défini par :}$$

$$J(u) = I(u) - \frac{1}{\frac{dE}{dx}} Y(u)$$

est égale à $\frac{u_0}{2 \frac{dE}{dx}}$ soit $\frac{x_0}{2}$, valeur identique à celle trouvée précédemment dans le cas général.

2) Densité de probabilité Γ

En fait on peut se demander s'il n'est pas préférable de prendre pour $g(u, x)$ une fonction quelconque qui satisfasse aux propriétés suivantes :

$$\left. \begin{aligned} g(u, x) &\geq 0 \quad \forall u > 0 \quad \text{et} \quad \forall x > 0 \\ g(u, x) &= 0 \quad \text{pour} \quad u < 0 \quad \forall x > 0 \\ g(u, 0) &= \delta(u) \\ \int_0^\infty g(u, x) du &= 1 \\ \mu_1 &= \int_0^\infty u g(u, x) du = \frac{dE}{dx} x \\ \mu_2 &= \int_0^\infty (u - \mu_1)^2 g(u, x) du = S^2 x \end{aligned} \right\} \quad (76)$$

Ainsi si l'on considère la fonction (densité de probabilité Γ d'après Lukacs) :

$$g(u, x) = \frac{\alpha (\alpha u)^\lambda e^{-\alpha u}}{\Gamma(\lambda + 1)}$$

qui a pour transformée de Laplace (pour $\lambda > -1$) :

$$G(p, x) = \frac{\alpha^{\lambda+1}}{(p + \alpha)^{\lambda+1}} = e^{-(\lambda+1)[\log(p+\alpha) - \log \alpha]} \quad (77)$$

nous pouvons identifier les deux premiers moments centrés afin de déterminer les paramètres α et λ . Remarquons que $g(u, x)$ est normé car $G(0, x) = 1$.

Nous avons :

$$\left. \begin{aligned} \mu_1 &= \frac{\lambda+1}{\alpha} \\ \mu_2 &= \frac{\lambda+1}{\alpha^2} \\ \mu_3 &= 2 \frac{\lambda+1}{\alpha^3} \end{aligned} \right\} \quad (78)$$

D'après (76) et (78), on obtient :

$$\begin{cases} \lambda+1 = \frac{\left(\frac{dE}{d\alpha}\right)^2}{S^2} \alpha \\ \alpha = \frac{\frac{dE}{d\alpha}}{S^2} \end{cases}$$

D'après (71) et (72), ceci peut encore s'écrire :

$$\begin{cases} \lambda+1 = \frac{x}{x_0} \\ \alpha = \frac{1}{u_0} \end{cases}$$

Nous obtenons alors pour $g(u, x)$:

$$g(u, x) = \frac{1}{u_0} \frac{\left(\frac{x}{x_0}\right)^{\frac{x}{x_0}-1}}{\Gamma\left(\frac{x}{x_0}\right)} e^{-\frac{x}{u_0}} \quad (79)$$

et sa transformée de Laplace :

$$G(p, x) = e^{\frac{x}{x_0} \cdot \text{Log}\left(\frac{1}{u_0 p + 1}\right)} \quad (80)$$

Calculons le coefficient de dissymétrie de cette densité $g(u, x)$:

$$D = \frac{\mu_3}{\mu_2^{3/2}} = \frac{2\sqrt{x_0}}{\sqrt{x}} \quad (81)$$

Si l'on pose $t = \frac{x}{x_0} - 1$, on a :

$$I(u) = \frac{1}{\frac{dE}{dx}} e^{-\frac{u}{u_0}} \int_{-1}^{\infty} \frac{\left(\frac{u}{u_0}\right)^t}{\Gamma(t+1)} dt$$

Or on trouve dans Erdelyi la fonction $V(x, a)$ définie comme suit :

$$V(x, a) = \int_a^{\infty} \frac{x^t dt}{\Gamma(t+1)} = \int_0^{\infty} \frac{x^{t+a} dt}{\Gamma(t+a+1)}$$

ainsi on peut écrire :

$$I(u) = \frac{1}{\frac{dE}{dx}} e^{-\frac{u}{u_0}} V\left(\frac{u}{u_0}, -1\right)$$

III. COURBE D'EXCITATION THEORIQUE POUR UN PROFIL C(x) DONNE

Le problème consiste ici à calculer l'équation (3a). Pour ce faire, nous avons à notre disposition plusieurs formulations possibles.

i) en premier lieu, on décompose la cible en tranches successives d'épaisseur mince ε , on peut alors définir la suite des C_n par :

$$C_n = \int_{(n-1)\varepsilon}^{n\varepsilon} C(x) dx \simeq \varepsilon C(n\varepsilon) \text{ pour } 1 \leq n \leq N \quad (82)$$

Soit $N^{\varepsilon}(E_0)$ la courbe d'excitation expérimentale obtenue sur une cible mince homogène d'épaisseur ε et de même nature que la cible ayant le profil $C(x)$ inconnu. On peut alors calculer la courbe d'excitation théorique $N(E_0)$ correspondant au profil $C(x)$ en appliquant la relation (14). Il vient alors :

$$N(E_0) = N^{\varepsilon}(E_0) * \left[C_1 \delta(E_0) + C_2 g(E_0, \varepsilon) + \dots \right. \\ \left. \dots + C_n g(E_0, (n-1)\varepsilon) + \dots \right]$$

que nous pouvons encore écrire sous la forme :

$$\left. \begin{aligned} N(E_0) &= N^{\varepsilon}(E_0) \cdot C_1 + N^{\varepsilon}(E_0) * V(E_0) \\ \text{où } V(E_0) &= \sum_{n=2}^N C_n g(E_0, (n-1)\varepsilon) \end{aligned} \right\} \quad (83)$$

Cette formulation implique la connaissance des fonctions $g(u, x)$.

ii) La deuxième formulation implique la connaissance de la section efficace et de la dispersion en énergie du faisceau contenues dans $\bar{\sigma}_0(E_0)$ et de la fonction $I_X(u)$ définie par :

$$I_X(u) = \int_0^x g(u, x) dx$$

On peut écrire alors :

$$N(E_0) = \bar{\sigma}_0(E_0) * W(E_0) \quad (84)$$

où

$$W(E_0) = C_1 I_{\varepsilon}(E_0) + C_2 [I_{2\varepsilon}(E_0) - I_{\varepsilon}(E_0)] + \dots + C_N [I_{N\varepsilon}(E_0) - I_{(N-1)\varepsilon}(E_0)]$$

Les C_n sont définis par (82). On obtient alors :

$$W(E_0) = (C_1 - C_2) I_{\varepsilon}(E_0) + (C_2 - C_3) I_{2\varepsilon}(E_0) + \dots + C_N I_{N\varepsilon}(E_0)$$

iii) La troisième formulation implique la connaissance de la section efficace et de la dispersion en énergie du faisceau ainsi que de la fonction d'interaction primaire $f(u)$ et de ses autoconvoluées successives. On utilise ici la relation (46) qui donne :

$$N(E_0) = \bar{U}_0(E_0) * \sum_{n=0}^{\infty} S_n(m) \frac{m^n}{n!} f(E_0)^{*n} \quad (85)$$

où

$$S_n(m) = \int_0^{\infty} C(x) x^n e^{-mx} dx$$

. Pour la suite il convient de distinguer deux cas selon la valeur de la largeur de la résonance (Γ_R) par rapport à la valeur de u_{MAX} définie par (20).

A) Résonance large ($\Gamma_R > u_{MAX}$)

. Nous avons mis au point un programme de calcul qui permet de déterminer $N(E_0)$ pour un profil $C(x)$ donné et de comparer la courbe d'excitation ainsi trouvée à la courbe d'excitation expérimentale $S(E_0)$. On utilise dans ce programme la formulation (83) où nous avons pris pour $g(u, x)$ l'une des formes analytiques données précédemment (gaussienne ou fonction Γ).

. Pour effectuer ce calcul, il convient de se fixer la valeur des paramètres ε et N , compte tenu de la largeur Γ_R de la résonance et de l'excursion ΔE envisagée lors du tracé de la courbe d'excitation. Le choix de ε est guidé par la valeur de Γ_R de telle sorte que l'on ait :

$$\frac{d\Gamma}{dx} \cdot \varepsilon \ll \Gamma_R$$

La valeur maximum ΔE de l'excursion en énergie fixe l'épaisseur maximum analysée ($N\varepsilon$) ; on doit avoir, en effet :

$$\int_{\Delta E}^{\infty} g(u, N^E) du \ll 1$$

Soit E_1 la valeur de l'énergie correspondant à l'énergie de départ pour la courbe d'excitation $N(E_0)$. Notons que cette valeur doit être légèrement inférieure à l'énergie E_R de la résonance. Le calcul de la courbe d'excitation théorique $N(E_0)$ pour $E_0 \in [E_1, E_1 + \Delta E]$ implique d'après (83) la connaissance de $N(E_0)$ pour $E_0 \in [E_1 - \Delta E, E_1 + \Delta E]$. Cette courbe $N^E(E_0)$ est relevée expérimentalement avec un pas en énergie Δu petit devant E_R . On écrira dans la suite $N^E(E_0)$ sous la forme d'une suite $N^E(l)$ où l est un nombre entier et tel que :

$$E_0 = (E_1 - \Delta E) + l \Delta u$$

$$l \text{ entier} \in [1, 2L] \quad \text{où } L = \frac{E_1}{\Delta u}$$

On calcule alors le noyau $V(E_0)$ définie par (83) sous la forme d'une suite de nombre $V(l)$ telle que

$$E_0 = l \Delta u \quad \text{où } l \in [1, L]$$

$$V(l) = \sum_{n=2}^n C_n g(l \Delta u, (n-1)\epsilon)$$

On peut calculer alors la courbe d'excitation théorique $N(E_0)$ pour E_0 variant de E_1 à $E_1 + \Delta E$, avec un pas énergétique Δu ; on obtient d'après (83)

$$N(E_0(i)) = C_1 N^E(i) + \sum_{l=1}^{L-1} N^E(i-l) V(l)$$

pour $i \in [L, 2L]$

où $E_0(i) = E_1 + i \Delta u$

En fait on pourrait s'arrêter à ce stade ; néanmoins nous avons "raffiné" le programme de calcul

de telle sorte que l'on ait la courbe d'excitation théorique $N(E_0)$ en tout point comparable à la courbe expérimentale $S(E_0)$ recueillie sur la cible de profil inconnue.

Nous obtenons la courbe expérimentale $S(E_0)$ pour

$$E_S < E_0 < E_S + \Delta E_S \quad \text{où } E_S \gg E_1$$

et $E_S + \Delta E_S \leq E_1 + \Delta E$ avec un pas en énergie

Δu_S supérieure en général (ou égale) à Δu . Il convient alors d'exprimer $N(E_0)$ avec le même pas en énergie que $S(E_0)$ soit Δu_S . Pour ce faire nous utilisons un programme d'interpolation qui nous donne la nouvelle courbe théorique $N^S(E_0)$ avec le pas Δu_S . Ensuite il convient de normaliser les deux courbes ; pour cela nous calculons les sommes suivantes :

$$A = \sum_{j=1}^J N^S(E_0(j))$$

$$B = \sum_{j=1}^J S(E_0(j))$$

où $E_0(j) = E_S + j \Delta u_S$

et $J = \frac{\Delta E_S}{\Delta u_S}$

Les courbes $\bar{N}^S(E_0)$ et $\bar{S}(E_0)$ définies par

$$\bar{N}^S(E_0) = \frac{100}{A} N^S(E_0)$$

$$\bar{S}(E_0) = \frac{100}{B} S(E_0)$$

sont alors en principe directement superposables ; (elles correspondent toutes deux à 100 coups par canal en moyenne). Notons que la valeur du rapport B/A permet d'estimer la valeur absolue de $C(x)$ compte tenu des conditions expérimentales (nombre de particules incidentes, angle solide de détection) utilisées lors de la mesure de la courbe $S(E_0)$.

1) Application à la résonance $O^{18}(p,\alpha)N^{15}$
à 629 keV ($\Gamma_R \approx 2,5$ keV)

La courbe $N^C(E_0)$ est obtenue sur un oxyde anodique de 50 Å d'épaisseur (nous n'avons pas observé de différence entre Al_2O_3 et Ta_2O_5 sur la forme de $N^C(E_0)$) avec un pas en énergie $\Delta u = 0,2$ keV. Nous avons ainsi plus de dix points dans la mi-hauteur du pic de résonance. L'épaisseur de 50 Å d'oxyde correspond sensiblement à une perte d'énergie de 0,4 keV pour les protons de 650 keV. L'excursion en énergie ΔE n'excède pas 40 keV. Ceci fixe l'épaisseur maximum analysée à 2700 Å. Nous fixons l'énergie E_+ à 620 keV soit 9 keV en dessous de l'énergie de résonance. Ainsi la courbe d'excitation de base $N^C(E_0)$ doit être connue de 580 keV à 660 keV avec un pas de 0,2 keV.

a) Transport de l'oxygène au cours de la croissance de film anodique.

. L'analyse de la courbe d'excitation observée sur une couche d'oxyde anodique constitué d'un "sandwich" (formé en O^{18} puis en O^{16}) permet de déterminer si l'ordre des atomes d'oxygène reste conservé. Nous avons ainsi montré que, pour l'aluminium et le tantale oxydé en solution aqueuse à forte densité de courant (≈ 1 mA/cm²), l'ordre des atomes d'oxygène reste conservé. Nous avons obtenu un excellent accord entre les courbes d'excitation théorique et les courbes d'excitation expérimentales. La figure 2 montre les courbes expérimentales obtenues respectivement sur un oxyde d'aluminium formé à 5 volts en solution enrichie en O^{18} et sur un oxyde initialement formé dans les mêmes conditions (5 volts dans une solution enrichie en O^{18}) puis réoxydé jusqu'à 55 V dans une solution de concentration isotopique naturelle. La courbe en trait continu correspond à la courbe d'excitation théorique calculée pour le

profil $C(x)$ indiqué.

La figure 3 représente la courbe d'excitation obtenue sur un oxyde de zirconium formé à 14 Volts en solution aqueuse de concentration isotopique naturelle puis réoxydé jusqu'à 48 Volts dans une solution enrichie en O^{18} . La courbe d'excitation montre clairement la présence d' O^{18} à l'interface oxyde-métal ainsi qu'à la surface de l'oxyde. Nous avons pu estimer le profil $C(x)$ des atomes d' O^{18} dans l'oxyde de zirconium comme le montre le bon accord observé entre la courbe théorique et la courbe expérimentale.

b) Autodiffusion de l'oxygène dans l'oxyde de zirconium

L'analyse du spectre des particules issues de la réaction permet d'étudier les profils de diffusion sur des profondeurs de l'ordre du micron. C'est ainsi que les spectres des particules α issues de la réaction $O^{18} (p, \alpha) N^{15}$ ont été relevés par des énergies de bombardement croissantes au voisinage de la résonance à 629 keV sur du zirconium oxydé en O^{16} à 800° C pendant 5 heures 30' puis placé sous O^{18} à la même température pendant 11'. La courbe reliant le maximum du spectre à l'énergie de bombardement constitue, en quelque sorte, une courbe d'excitation dont l'analyse donne des informations sur le profil dans les 2000 premiers Angstroms, le profil pour les plus grandes profondeurs étant obtenu par l'analyse du spectre des particules α issues de la réaction. Il ressort de l'analyse de cette courbe d'excitation (figure 4) que le profil d'autodiffusion de l'oxygène serait la somme de deux fonctions erfc :

$$C(x) = 7 \operatorname{erfc} \frac{x}{2 \times 0,03} + 3 \operatorname{erfc} \frac{x}{2 \times 0,11}$$

Seule l'analyse de la courbe d'excitation permet de mettre en évidence la variation rapide de $C(x)$ au voisinage de la surface. L'analyse du spectre des particules α émises permet de déterminer la variation lente de $C(x)$.

2) Application à la résonance $F^{19}(p, \alpha)O^{16}$
à 872 keV ($\Gamma_R \simeq 4,2$ keV)

Le programme de calcul de la courbe d'excitation théorique, mis au point pour la résonance $O^{18}(p, \alpha)N^{15}$ à 629 keV, a pu être appliqué à la résonance $F^{19}(p, \alpha)O^{16}$ à 872 keV. C'est ainsi que nous avons montré que les traces de fluor laissées par le polissage sur la surface du tantale, restent à l'interface métal-oxyde après oxydation de ce tantale poli.

B) Résonance fine ($\Gamma_R \ll u_{MAX}$)

Comme la courbe $N^e(E_o)$ dépend fortement de la nature de la cible, il est préférable pour le calcul de la courbe d'excitation d'utiliser la formulation donnée par l'équation (84) ou (85). Dans le cas où la largeur Γ_R de la résonance est faible vis à vis de la résolution en énergie du faisceau incident, on peut prendre pour fonction $\bar{\sigma}_0(E_o)$ la somme d'une Gaussienne centrée sur l'énergie de résonance et de largeur correspondant à la résolution du faisceau et d'une constante correspondant à la partie stationnaire de la section efficace. Le calcul de la courbe d'excitation théorique au voisinage des résonances $O^{18}(p, \alpha)N^{15}$ à 1165 keV et $Al^{27}(p, \alpha)Si^{28}$ à 992 keV est actuellement en cours.

LEGENDES DES FIGURES

Fig. 1 : Densité de probabilité $g(u,x)$ déterminé par la méthode de Monte-Carlo pour $x = 907 \text{ \AA}$ dans une cible d' Al_2O_3 et pour des protons incidents de 650 keV. Le calcul est effectué pour un nombre moyen d'interactions égale à 10 (dans l'approximation de la perte continue) et pour un nombre d'évènements égal à 5000.

Fig. 2 : Courbes d'excitation (0,54 keV/canal) au voisinage de la résonance $^{18}\text{O}(p,\alpha)^{15}\text{N}$ à 629 keV obtenue sur une cible d'oxyde anodique d'aluminium :

○ formé à 5 Volts dans une solution aqueuse enrichie en ^{18}O

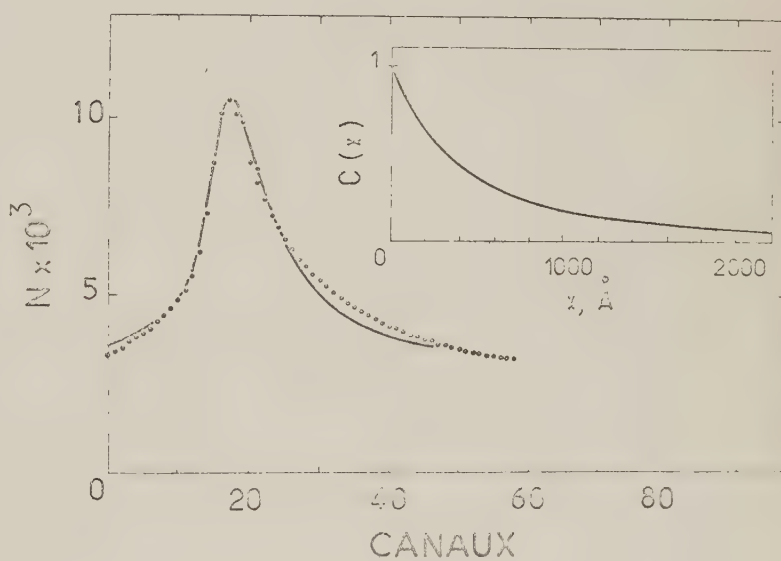
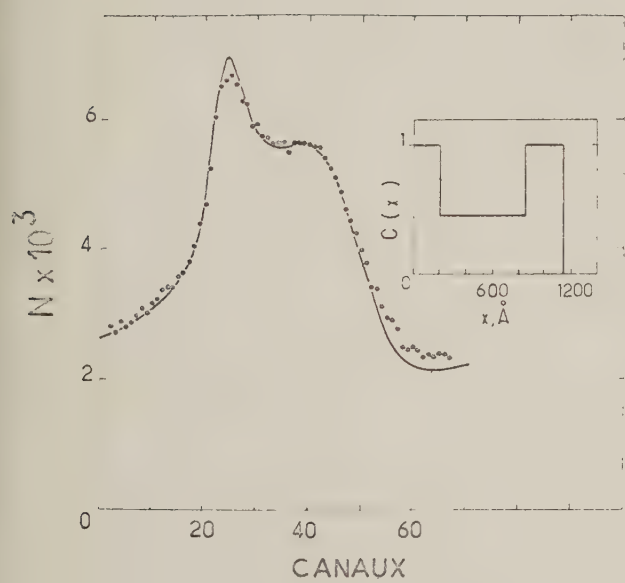
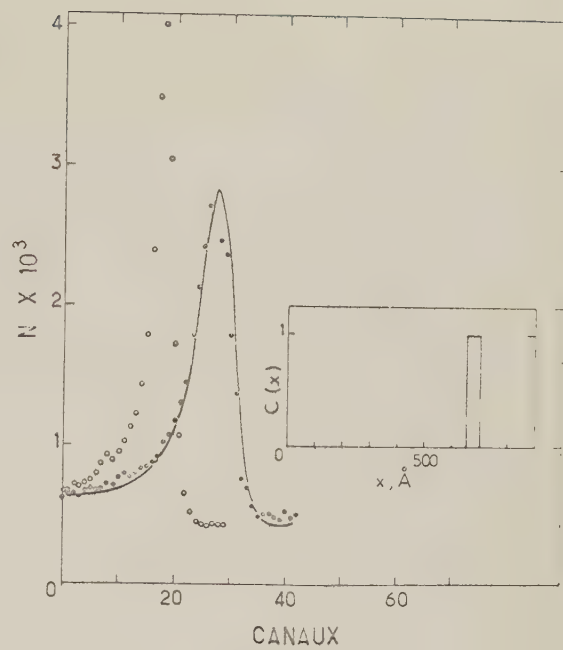
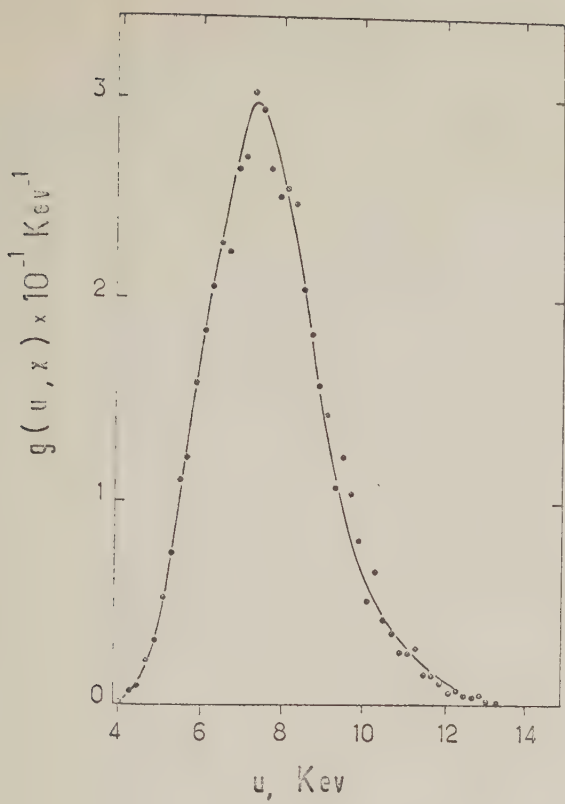
○ formé à 5 Volts dans une solution aqueuse enrichie en ^{18}O puis réoxydé à 55 Volts dans une solution de concentration isotopique naturelle.

La courbe d'excitation en trait continu est obtenue par le calcul pour le profil $C(x)$ indiqué.

Fig. 3 : Courbe d'excitation (0,375 keV/canal) au voisinage de la résonance $^{18}\text{O}(p,\alpha)^{15}\text{N}$ à 629 keV obtenue sur une cible d'oxyde anodique de zirconium formé à 14 Volts en solution de concentration isotopique naturelle puis réoxydé à 48 Volts en solution enrichie en ^{18}O . La courbe d'excitation en trait continu est obtenue par le calcul pour le profil $C(x)$ indiqué.

Fig. 4 : Courbe d'excitation ($0,5 \text{ keV/canal}$) au voisinage de la résonance $O^{18} (p, \alpha) N^{15}$ à 629 keV obtenue sur une cible d'oxyde thermique de zirconium, oxydé en O^{16} à 800° C pendant 5 h 30' puis placé sous O^{18} à la même température pendant 11'.

La courbe d'excitation en trait continu est obtenue par le calcul pour le profil $C(x)$ indiqué.



REFERENCES

- A. BLANC-LAPIERRE., "Modèles statistiques pour l'étude de phénomènes de fluctuations", Masson, PARIS, 1963, P.41.
- R.O. BONDELID et J.W. BUTLER., Phys. Rev. Vol 130, No 3, p.1078 - 1090, May 1963.
- A. ERDELYI, W.MAGNUS, F. OBERHETTINGER, and F.G. TRICOMI., Higher Transcendental Functions (H.T.F.) (Mc Graw-Hill Book Company, Inc, New-York, 1953) Vol III, P.222.
- H.E. GOVE., "Nuclear reactions" édité par P.M. Endt and M. Demeur (North Holland publishing company - Amsterdam) 1959, Vol I, chap. VI.
- E. LUKACS., "Characteristic functions" Charles Griffin and Cie, London 1960, P.78.
- M. SAUCE., Communication privée.
- W.T. SCOTT., Rev. Mod. Phys. Vol 35, P.231, April 1963.

